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Coke Quench Tower Emission Testing Program

York Research Corp, Stamford, CT

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Coke Quench Tower Emission Testing Program

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16. ABSTRACT

The report gives results of a field study to further define quench tower organic emissions, the character and magnitude of which are virtually unknown. (Limited testing in 1976 indicated that a large quantity of organic material was emitted from quench towers, but these data were inconclusive because so few samples were analyzed.) Sufficient stack samples were taken under controlled coke and quench water quality conditions to provide a statistically confident basis for emission factor determination. The samples were subjected to extensive organic chemical analysis for identification and quantification of similar functional groups and selected individual compounds known or expected to be carcinogenic. Fifty-three organic compounds were found in quench tower emissions; seven in sufficient quantity to be considered potential health hazards. The use of waste water from other coke plant sources for quenching greatly increases the organic load when compared to quenching with river water. Although the water itself is the principal source of organic emissions, the coke also appears to contribute. The majority of organics detected are either gaseous or associated with small particles, so they will contribute to ambient air loads beyond plant boundaries.

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Coking	Carcinogens	Stationary Sources	13H	06E
Quenching				
Testing			14B	
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1.0 SUMMARY

York Research Corporation was contracted by the Environmental Protection Agency to conduct a study of coke quench tower organic emissions. Testing was conducted at quench tower No. 1, U.S. Steel's Lorain Works, Lorain, Ohio in November, 1977. The primary objectives of the study were to:

- Characterize and quantify the organic matter in coke quench tower emissions
- Identify the possible origins of organic emissions by evaluating the effects of various process conditions (quench water and coke) on organic emissions.

Stack samples were collected by modified EPA Method 5 sampling methods and subjected to extensive organic chemical analysis for identification and quantification of individual organic compounds. Sufficient samples were taken under controlled process conditions to provide a statistically confident basis for emission factor determination. The process conditions under consideration were clean quench water, contaminated quench water (flushing liquor and blowdown from other plant processes), green coke (not fully distilled) and nongreen coke.

Supplemental objectives of the test program were the following:

- Determine the total organic carbon content of the quench water in order to study the mass balance around the quench tower.
- Determine the amount of benzene soluble material in coke quench tower emissions.
- Measure benzene and total hydrocarbons in the stack aerosol (2 samples).
- Obtain a stack sample for bioassay.

1.1 Organic Emissions

Fifteen tests were performed for the determination of quench tower organic emissions: six with clean water and nongreen coke, five with clean water and green coke, and four with contaminated water and nongreen coke. The test results are summarized in Table 1-1, showing the large quantities of Polycyclic Aromatic Hydrocarbons (PAH) and certain polar compounds (heterocyclic oxygen and nitrogen compounds) found in the quench tower plume. Together, these organic classes represent fifty-three different organic species detected in emissions samples. Those species found at the highest concentrations include:

1) Naphthalene
2) Methyl Naphthalenes
3) Acenaphthylene/Biphenylene
4) Dimethyl Naphthalenes
5) Fluorene
6) Dibenzofuran/Methyl Biphenyl
7) Anthracene/Phenanthrene
8) Methyl Anthracenes
9) Phenol
10) Cresol
11) Methyl Cresol
12) Quinoline

It may be observed in Table 1-1 that the concentration of organics is much greater in the contaminated water tests than in the clean water tests. Also, the clean water - green coke tests show higher organic concentrations than the clean water - nongreen coke tests.

A specific analysis for benzo (a) pyrene (BaP) in the organic emission samples was performed and revealed substantial amounts of BaP to be present (see Table 1-1). Although BaP levels are consistently higher in the contaminated water tests than in the clean water tests, the data were scattered in regards to coke greenness. BaP was not detected in every test but when it was its concentration exceeded the Minimum Acute Toxicity Effluent values.(16)

TABLE 1-1

SUMMARY OF COKE QUENCH TOWER ORGANIC EMISSIONS

	Clean Water		Contaminated Water	
	ug/m³	g/metric ton of coal	ug/m³	g/metric ton of coal
PAH				
All Tests	767[a] (170 to 1,900)[b]	0.758 (0.156 to 1.90)	31,000 (13,700 to 47,300)	32.1 (15.5 to 46.4)
Green Coke Tests	1160 (660-1900)	1.17 (0.679 to 1.90)	--	--
Nongreen Coke Tests	442 (170 to 745)	0.419 (0.156 to 0.646)	31,000 (13,700 to 47,300)	32.1 15.5 to 46.4)
Polar Compounds Total[c]				
All Tests	771 (60 to 6090)	1.10 (0.0575 to 6.89)	540,000 (243,000 to 922,000)	581 (185 to 1009)
Green Coke Tests	1540 (118 to 6090)	1.70 (0.119 to 6.89)		
Nongreen Coke Tests	134 (60 to 253)	0.606 (0.0575 to 3.13)	540,000 (243,000 to 922,000)	581 (185 to 1009)
Benzo (a) Pyrene				
All tests	19 (ND[e] to 66)	0.019 (ND to 0.072)	76 (36 to 99)	0.081 (0.040 to 0.12)
Green Coke Tests	13 (ND to 66)	0.012 (ND to 0.060)	--	--
Nongreen Coke Tests	24 (ND to 66)	0.024 (ND to 0.072)	76 (36 to 99)	0.081 (0.040 to 0.12)

---

[a] Average value.
[b] (Range)
[c] Pht
[d] Results from an analysis specific for benzo (a) pyrene which is separate from the PAH analysis above.
[e] ND = Not Detected.

Each of three organic emission tests were analyzed according to three separate sections of the sampling train. These results indicated that most of the PAH found for each test was in the organic adsorber unit, which means this material is either vaporous or associated with particles smaller than 0.3 micrometers.

A comparison of the organic emissions data with various rating systems showed that the following compounds considered to be toxic, hazardous, or carcinogenic (17,18) are present in the quench tower plume:

1) Benzo (a) pyrene
2) 3-Methyl cholanthrene
3) 7, 12-Dimethyl benz (a) anthracene
4) Dibenz (a,h) anthracene
5) Dibenzo (a,h) pyrene
6) Dibenzo (a,i) pyrene
7) Benz (a) anthracene (s)
8) Pyridine
9) Indeno (1,2,3-cd) pyrene
10) Phenanthrene
11) Phenol
12) Cresol
13) Quinoline

Silicone grease and phthalates were detected in the organic emissions samples in large amounts. These substances are considered to be sample contaminants but their origin and method of entry into the test samples is not well defined. Silicone grease was used to seal some glass connections in the back half of the sampling train, however, its appearance in a front half sample (cyclone) and in some water samples and blanks indicates that another source may have been present. Phthalates were found in all of the organic emissions tests and in consistently greater quantities in contaminated water tests than in clean water tests. Phthalates have also been found in other tests of quench tower emissions and coke oven door leaks.(1,24) Due to these findings it has been speculated that phthalates could originate from coke oven processes.

1.2 Organics in Quench Water

Quench water samples were found to contain many of the same organic species present in quench tower emissions. It was observed that as the molecular weights of the species increases, the ratio of the quantity of a species in the stack emission to the quantity introduced in the makeup liquor becomes less and less. The lower the molecular weight the higher the boiling point, therefore, the lower molecular weight species are readily stripped from the quench water by the evaporation and distillation process of the quench. In a similar manner, the contaminated makeup liquor is stripped of lower molecular weight species and the higher molecular weight species tend to remain in the quench water. A few of the higher molecular weight compounds do not even appear in the stack emissions, however, almost all of the other species are present in the stack emissions in equivalent or larger quantities than found in the makeup water.

Samples of clean and contaminated quench water were taken and analyzed for Total Organic Carbon (T.O.C.). A mass balance around the coke quench tower reveals that of those individual organic compounds which were measured there were greater quantities found in the stack emissions than came in via the makeup water. Coke is suspected as an additional source of these organic emissions.

1.3 The Source of Quench Tower Organic Emissions

A statistical analysis of the organic emissions data showed that there is a significant realtionship between the three different test conditions of: clean water and green coke, clean water and nongreen coke, and contaminated water and nongreen coke; and the concentration of total PAH and most individual organic compounds in coke quench tower emissions. The concentration of organics in the quench tower plume increases when contaminated water is used to quench. The organic emissions also increase with the quenching of greener coke. The effect of quench water quality is much greater than the effect of coke greenness.

1.4 Benzene Soluble Residue, Benzene, and Total Hydrocarbons

Benzene soluble residue in coke quench tower emissions was determined for three tests. A substantial amount of benzene solubles (at least 234 grams per metric ton of coal) was found, with the greater quantity collected in the adsorber.

Two grab samples of quench tower emissions were taken and analyzed for benzene and Total Hydrocarbons (THC). With clean quench water in use, 0.005 ppm and 0.040 ppm benzene and 8.54 ppm and 17.34 ppm THC were detected.

1.5 Biological Test

A high volume sample of coke quench tower emissions was taken with clean quench water in use. This sample was subjected to several bioassays by Litton Bionetics. The Ames bacterial assay was run with and without metabolic activation using rat liver extract and showed the quench tower emission sample was not mutagenic under these conditions. The results of toxicity tests employing the same bacterial strains were also negative.

The clonal cytotoxicity assay was performed on the emission sample in order to determine the sample's potential cytoxicity through its effect on the colony forming ability of cultured Chinese hamster cells (CHO). A sample concentration between 74 and 100 µl/ml reduced the number of colonies by 50% (EC50 value). Compared with a standard range for low toxicity of 60 to 600 µl/ml the quench tower emission sample was determined to be of low toxicity.

1.6 Particulate Emissions

The organic emission tests and benzene soluble residue tests were also analyzed for particulate. These test results are summarized in Table 1-2. There was a striking reduction in the quantity of particulate emissions when the switch was made from contaminated to clean quench water. As shown in Table 1-2, the front half emission was reduced from 1.1 kg per metric ton of coal during the contaminated water tests to 0.68 kg per metric ton of coal during the clean water tests.

Although carloads of green coke are smoky and emit much particulate, there seems to be no correlation of coke greenness to the concentration of particulate in the stack aerosol. One possible explanation for this dramatic reduction in quench tower emissions from green cars is the scrubbing mechanism taking place when the top layers of coke are cooled and then wetted by the continued spraying of the quench water. This reduction in plume particulate minimizes the effect of coke greenness on stack emissions.

The weight of larger particles collected by the cyclone is about 45% of the total weight emitted when quenching with clean water and about 75% of the contaminated water quench emission. The average size of the particulate in the plume aerosol was less than 4 micrometers in previous tests at Lorain(1) but this would be shifted towards a larger size in the present study due to the greater cyclone collection.

The particulate results for the benzene soluble residue tests are shown in Table 1-2 to be only half that found for the front half in the organic emission tests.

TABLE 1-2

SUMMARY OF COKE QUENCH TOWER PARTICULATE EMISSIONS
(in kg/metric ton of coal)

Organic Emission Tests

	CLEAN QUENCH WATER		CONTAMINATED QUENCH WATER	
	Nongreen Coke	Green Coke	Nongreen Coke	Green Coke
Cyclone	0.32	0.29	0.89	-
Probe/Nozzle	0.15	0.039	0.10	-
Filter	0.32	0.29	0.16	-
Total Front Half	0.79	0.62	1.1	-

	Total Clean Tests	Total Contaminated Tests
Cyclone	0.30	0.89
Probe/Nozzle	0.075	0.10
Filter	0.30	0.16
Total Front Half	0.68	1.1

Benzene Soluble Residue Tests

	Clean Water-Green Coke	Contaminated Water Nongreen Coke
Cyclone	0.26	0.42
Probe/Nozzle	0.042	0.033
Filter	0.0044	0.038
Subtotal-Front Half	0.31	0.49
Total (including front half, condenser, adsorber)	0.52	0.99

2.0 CONCLUSIONS

The organic emissions from the coke quench tower tested were found to be substantial. Polycyclic aromatic hydrocarbon emissions ranged from 0.15 to 46 grams per metric ton of coal and polar compound totals ranged from 0.057 to 1000 grams per metric ton of coal. Most of these organics are either vaporous or associated with particles smaller than 0.3 micrometers.

Bioassays of one coke quench tower emission sample were negative for mutagenicity and toxicity, and showed the sample to be of low cytotoxicity. However, out of fifty-three different organic species detected in quench tower emissions, thirteen have been designated as either toxic, hazardous, or carcinogenic.(17,18) Among these potentially harmful species is benzo (a) pyrene, which although not detected in all tests, was found to exceed Minimum Acute Toxicity Effluent values for the concentrations measured.

The process conditions of quench water quality and coke greenness have a definite effect on organic emissions from the quench tower. The use of contaminated quench water rather than clean water increases the average PAH concentration 40 times while the average concentration of polar materials increases 500 times. The quenching of green coke rather than nongreen coke increases both PAH and polar compound emissions by a factor of 3. The quality of the quench water has a decidedly greater effect on the quantity of organic emissions than does coke greenness. These conclusions are supported by statistical analysis of the data.

Particulate emissions from the coke quench tower are also substantial, ranging from 290 to 1220 grams per metric ton of coal. Again, quench water quality has a great effect on the quantity of particulate emitted, with an average of 680 grams per metric ton of coal for clean water increasing to an average of 1200 grams per metric ton of coal for contaminated water. The quality of the coke being quenched did not appear to have any effect on the amount of particulate emissions.

3.0 RECOMMENDATIONS

Large quantities of silicone grease and phthalates were found in the coke quench tower emission samples and the presence of these substances interfered with the determination of total organics. In addition, there is much uncertainty as to the origin of these compounds. For these reasons it is recommended that all sources of phthalates and silicone grease in the coking and quenching processes be determined prior to another test program for quench tower organic emissions. It is also recommended that all use of silicone grease on sampling equipment be avoided in similar tests and that other methods (i.e. teflon sleeves) be used to obtain tight seals between train components.

4.0 INTRODUCTION

It has been a common practice in the U.S. steel industry to use contaminated water in the quenching of incandescent coke, that is, water contaminated by prior use in either quenching or other processes within the plant. Typically, 10-20 ton loads of hot coke (upwards of 2000°F) are quenched by 6,000 to 12,000 gallons of water. Each quench takes 2-3 minutes and produces huge billowing clouds of steam, water droplets, and air contaminants. In order to draft these emissions out of the work area quenching takes place under towers which are open at the bottom to admit the coke car. Baffles are often fitted inside the towers in order to reduce the amount of large diameter particles emitted, and at the same time reduce water losses and thus the amount of makeup water required.

It had been theorized that significant amounts of coke quench water contaminants are transformed by the quenching process into air pollutants which pass through baffles and enter the atmosphere.(4) Studies performed by York Research Corporation (YRC) quantified particulate emissions under varied conditions of quench water quality and also found certain gaseous emissions and organic material to be present in the stack aerosol. However, major consideration had not been given to these organic emissions or to the effect of the varied process condition of coke greenness. Thus, York Research Corporation was contracted by the U.S. Environmental Protection Agency to further evaluate the coke quench operation particularly concerning organic emissions and identification of the source of these pollutants.

The site selected for the coke quench tower emissions testing program was U.S. Steel Company's Lorain Works, Lorain, Ohio, a fully integrated steel plant producing finished and semi-finished steel products. Since the previous quench tower work performed by YRC had been done at this site a broad data base for particulate and gaseous emissions, quench water flow rates and water contaminants already existed for use in support of a new test series. A wide range of coke greenness had been observed at this plant. In addition, a sampling methodology devised to handle the difficult test conditions presented by the quench had been successfully used in YRC's first test program. The coke quench tower emission study was conducted in November of 1977.

5.0 PROCESS DESCRIPTION

The integrated steel mill manufactures coke to be used as a basic raw material for the blast furnace. There are two generally accepted methods for manufacturing coke in this country. These are known as the beehive process and the by-product or chemical recovery process. This latter process produces about 99 percent of all metallurgical coke and is the process used at Lorain.

In the by-product coke manufacturing process, bituminous coal is heated in an oxygen-deficient atmosphere (coke oven) and volatile components of the coal are driven off. At the completion of this process the residue remaining in the oven is coke, the volatile components having been recovered and processed in the by-product plant to produce gas, tar, light oils, and other materials. The coke is removed from the oven and cooled by water sprays, after which it is stored for eventual use in the blast furnace.

Much of the following process description was taken from the 1976 study at Lorain.(1)

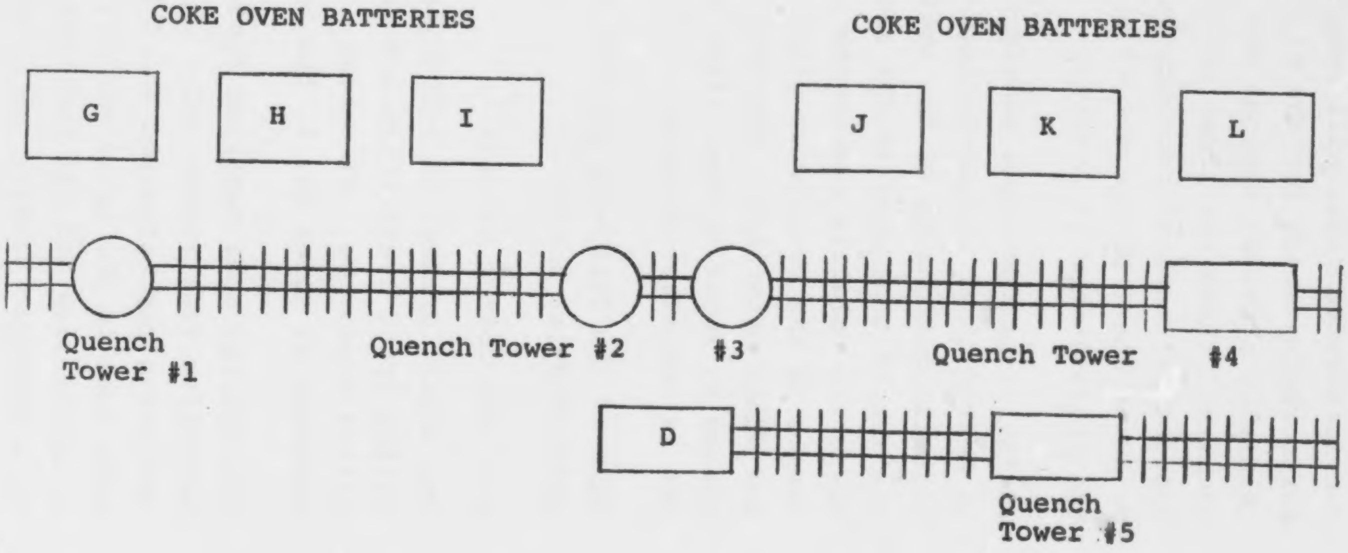
5.1 The Coking Process

The coking process is accomplished in narrow, rectangular, silica brick ovens which are arranged side-by-side in groups called batteries. At Lorain, G battery provided the coke quenched at tower No. 1, the test site.

The regular coal handling system is located between I and J batteries (see Figure 5-1). During the test period, H battery was being reconstructed and G battery could not be supplied with coal in the usual manner. Instead, coal was trucked to a nearby area and was supplied to G battery from ground level by a conveyor feeding the charge car.

FIGURE 5-1

COKE OVEN PLANT SCHEMATIC


COKE OVEN BATTERIES
COKE OVEN BATTERIES
G
H
I
J
K
L
Quench Tower #1
Quench Tower #2
#3
Quench Tower #4
D
Quench Tower #5

In order to charge the ovens, coal is loaded into a hopper car. This car holds approximately 13.1 tons of coal in three hoppers. At Lorain, there were scales for weighing the coal, but they were not used. After loading, the hopper car moves along the top of a battery where the coal is dumped through three ports in the oven top. This coal fills the oven to a point level with the top of the leveling bar door (oven density: 46-50 pounds per cubic foot). From 13.1 tons of coal per charge each oven yields:

		9.6 tons of coke oven product
	-	1.0 tons of breeze
Total =		8.6 tons furnace coke

The coke ovens at Lorain are 40 feet 1-3/4 inches long, 10 feet 1-7/8 inches high, 21 inches wide at the car end and 17 inches wide at the pusher end, averaging 19 inches in width. The working volume below the leveling bar is 560 cubic feet. There are 413 coke ovens in use in seven batteries, each battery consisting of 59 ovens. G battery was manufactured by Koppers and built in 1956. It was shut down temporarily in 1976 and its present condition is "rebuilt". The ovens are normally operated for three shifts per day, seven days per week, and convert upwards of 7,000 tons of coal per day to coke. Normal coking time is 17.3 hours. However, this may vary with the condition of the oven.

Typical oven temperatures were obtained from production records and some daily averages during the test period are listed in Table 5-1. The average coke oven temperature for G battery during the test period was 2338°F.

TABLE 5-1

AVERAGE OVEN TEMPERATURES (G BATTERY) DURING TEST PERIOD

Date	Average Oven Temperature (G Battery) ^{o}F
11/1/77	2337
11/2/77	2338
11/5/77	2352
11/6/77	2389
11/7/77	2360
11/8/77	2352
11/9/77	2346
11/10/77	2283
11/11/77	2284
11/15/77	2338
11/17/77	2286
11/19/77	2390
Average for test period	2338^{o}F

The coke ovens are separated from each other by a space between the walls of the adjacent ovens. Gas is burned in these spaces to provide the heat necessary for the coking process. This gas is about 40% of that produced from the coking process. The balance of the gas available from coking is used elsewhere in the steel plant. The combustion products from these inner wall furnaces are drafted out of the area by tall stacks. The ovens are operated under a very slight positive pressure so that any leakage occurs from the oven to the atmosphere or into the adjacent furnaces.

Three factors affecting the composition of the coke oven gases are:

- Coking temperature (this mostly determines the hydrogen to hydrocarbons ratio. The higher the temperature, the higher the hydrogen content of the gas and the lower the hydrocarbon content).

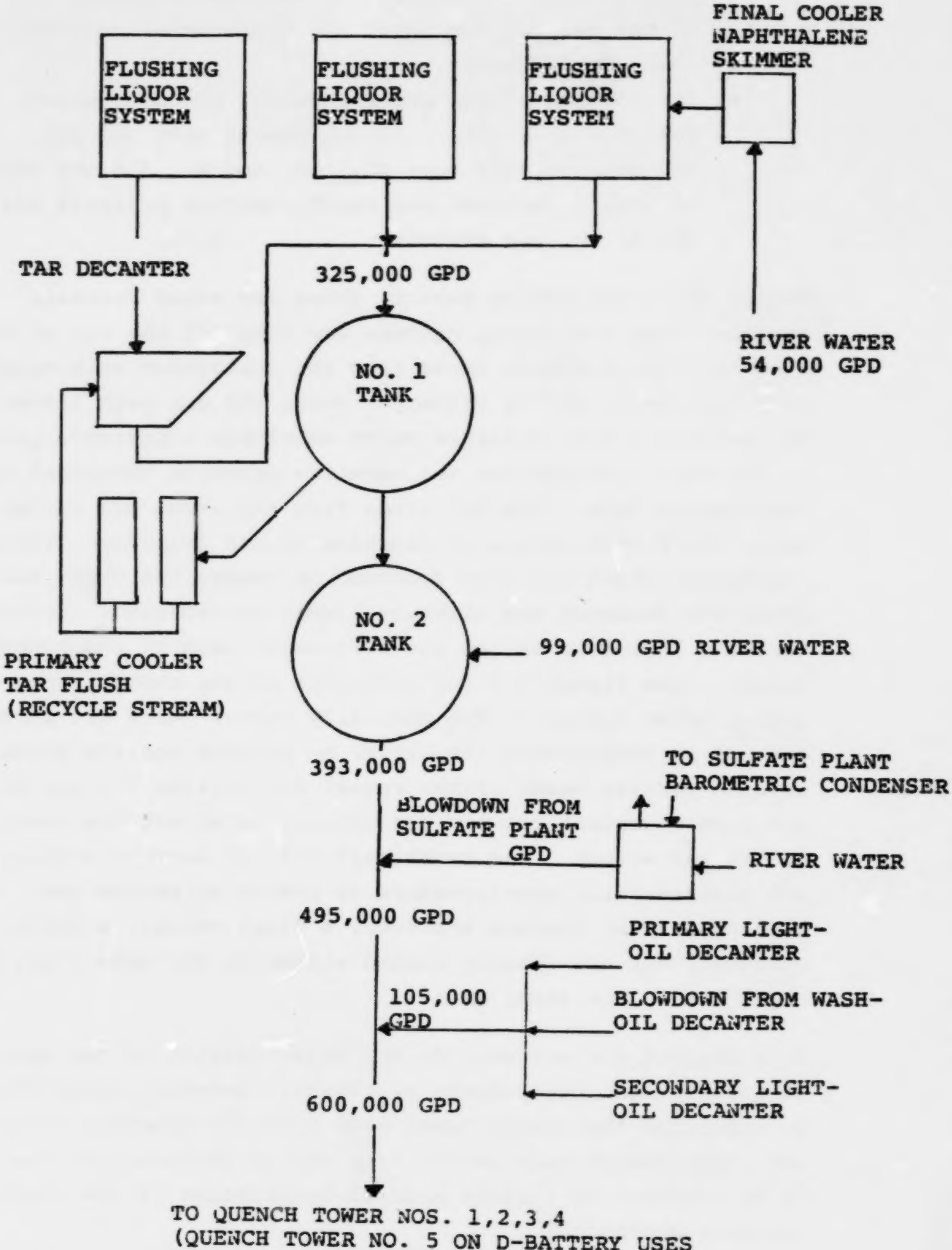
- Coal compositions.
- The amounts of air and combustion products drawn into the coke oven. Oxygen reacts with the gas and coke to form more CO_2, CO, and N. (In the case of Lorain the oven was under positive pressure and the effect was minimal.

During the total coking period, gases and other volatile material from the coking process are bled off the top of each oven through ascension pipes into the collection main which runs the length of the battery. Where the gas main leaves the battery a back pressure valve maintains a positive pressure on the oven side against the negative pressure developed by the exhaust fans. The hot gases from the ovens are cooled to below 212°F with sprays of flushing liquor (blowdown from plant processes) which are then decanted to remove the crude tar. After the decanter the flushing liquor is recycled. Excess flushing liquor is stored and eventually used at the quench tower. (See Figure 5-2 for a diagram of the contaminated quench water system.) The partially cooled gases are further reduced in temperature (to 110°F) by primary coolers which utilize service water (river water) for cooling the gas without direct contact between the cooling water and the chemicals in the gas stream. The gases pass through exhaust turbines and electrostatic precipitators to remove entrained tar. They then pass to an ammonia scrubber, a final cooler, a light oil scrubber, and are finally burned either in the coke plant or elsewhere in the steel mill.

This project did not include any investigation of the operations of the chemical by-products processes. However, since the make-up water for the quench tower sump included flushing liquors and other excess wash waters from the by-products process, it is appropriate to include a brief description of the chemical recovery operations.

FIGURE 5-2

DIAGRAM OF LORAIN COKE PLANT CONTAMINATED QUENCH WATER SYSTEM


FINAL COOLER NAPHTHALENE SKIMMER
FLUSHING LIQUOR SYSTEM
FLUSHING LIQUOR SYSTEM
FLUSHING LIQUOR SYSTEM
TAR DECANTER
325,000 GPD
RIVER WATER 54,000 GPD
NO. 1 TANK
NO. 2 TANK
99,000 GPD RIVER WATER
PRIMARY COOLER TAR FLUSH (RECYCLE STREAM)
393,000 GPD
TO SULFATE PLANT BAROMETRIC CONDENSER
BLOWDOWN FROM SULFATE PLANT GPD
RIVER WATER
495,000 GPD
PRIMARY LIGHT-OIL DECANTER
105,000 GPD
BLOWDOWN FROM WASH-OIL DECANTER
SECONDARY LIGHT-OIL DECANTER
600,000 GPD

TO QUENCH TOWER NOS. 1,2,3,4
(QUENCH TOWER NO. 5 ON D-BATTERY USES
ONLY RIVER WATER FOR QUENCHING)

Ammonia is recovered as an ammonium sulfate. Crude light oil and crude coal tar are also recovered. No tar distillation, phenol recovery or light oil purification is employed. All of the excess flushing liquors and blowdown from the ammonium sulfate plant are used to quench the coke produced in batteries G, H, I, J, K and L. D battery is normally quenched with river water. Figures 5-2 and 5-3 illustrate the various operations in the chemical by-product plant.

5.2 The Quenching Process

At the end of the coking period the doors are removed from each end of an oven and the pushing machine pushes the incandescent coke into the quenching car. The quench car is then moved by a small electric engine to the closest quench tower. (See Figures 5-4 and 5-5). At this point the car operator pulls a switch which activates a valve in the 16 inch pipe leading from the head tank to the spray nozzles. After a safety delay of about 15 seconds, 7-9 thousand gallons of water flow through a header and 10 nozzles onto the incandescent coke. Figures 5-6, 5-7, and 5-8 show photographs taken a few seconds apart through the first 20-30 seconds of the quench.

The hot coke is quickly cooled to about 250°F by the evaporation of about 20 percent of this water. Violent jets of superheated steam result from this process; and the steam, being less dense than the surrounding air, flows up the tower inducing a flow of cooler air through the car ports. Figures 5-9, 5-10, and 5-11 show the first eruption of steam, while 5-12 and 5-13 show the tower (stack) flow well established. During the rapid cooling, some of the coke fractures, and small particles are broken off and carried away by the gas and water stream. Some of the particles are ejected from the car as if by an explosion. The quench towers are built to contain the violence and turbulence of this cooling process, and the geometry of the tower directs most of this hot mixture of steam, air, water droplets,

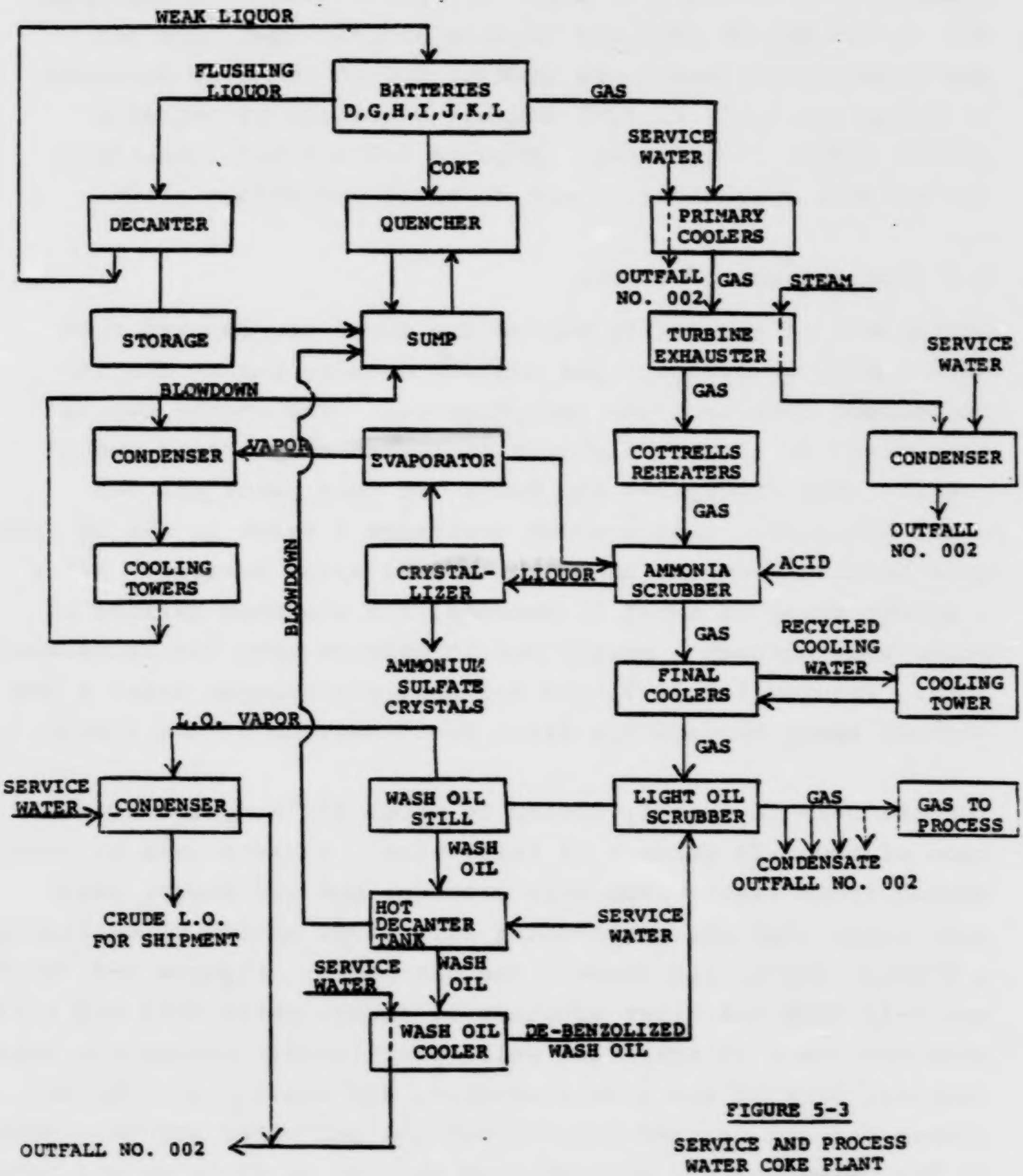

WEAK LIQUOR
FLUSHING LIQUOR
BATTERIES D,G,H,I,J,K,L
GAS
COKE
SERVICE WATER
DECANTER
QUENCHER
PRIMARY COOLERS
OUTFALL NO. 002
GAS
STEAM
STORAGE
SUMP
TURBINE EXHAUSTER
SERVICE WATER
BLOWDOWN
GAS
CONDENSER
VAPOR
EVAPORATOR
COTTRELLS REHEATERS
CONDENSER
OUTFALL NO. 002
GAS
COOLING TOWERS
BLOWDOWN
CRYSTAL-LIZER
LIQUOR
AMMONIA SCRUBBER
ACID
GAS
AMMONIUM SULFATE CRYSTALS
RECYCLED COOLING WATER
FINAL COOLERS
COOLING TOWER
L.O. VAPOR
GAS
SERVICE WATER
CONDENSER
WASH OIL STILL
LIGHT OIL SCRUBBER
GAS
GAS TO PROCESS
WASH OIL
CONDENSATE OUTFALL NO. 002
CRUDE L.O. FOR SHIPMENT
HOT DECANTER TANK
SERVICE WATER
SERVICE WATER
WASH OIL
WASH OIL COOLER
DE-BENZOLIZED WASH OIL
OUTFALL NO. 002

FIGURE 5-3

SERVICE AND PROCESS WATER COKE PLANT LORAIN WORKS

FIGURE 5-4
THE PUSH OF INCANDESCENT COKE
FROM THE OVEN TO THE QUENCH CAR

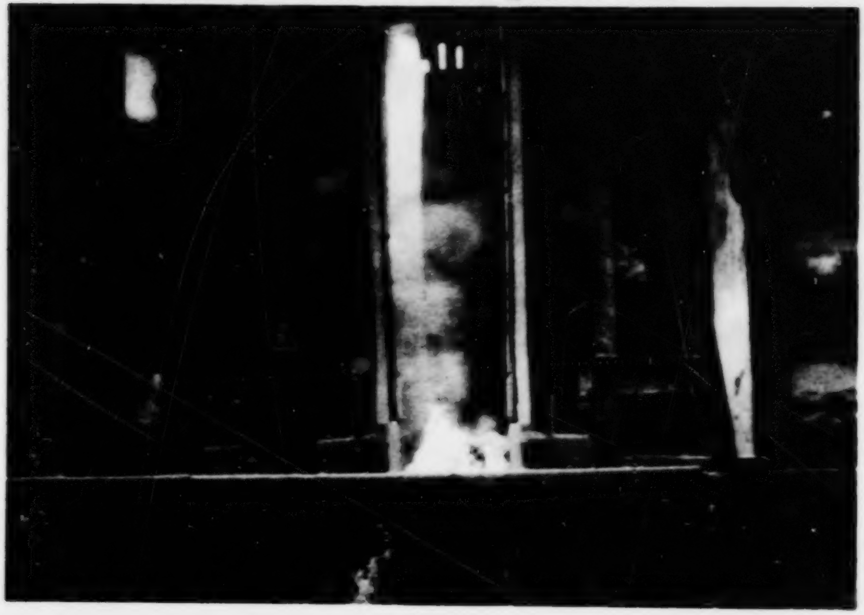


FIGURE 5-5
QUENCH CAR WITH INCANDESCENT
COKE ENTERING THE QUENCH TOWER

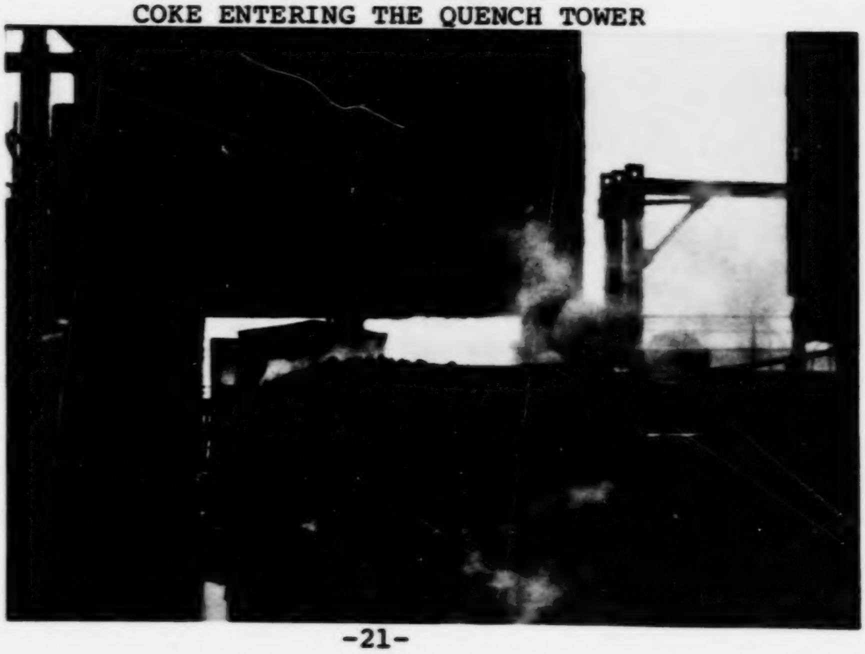


FIGURE 5-6
"CAR IN"

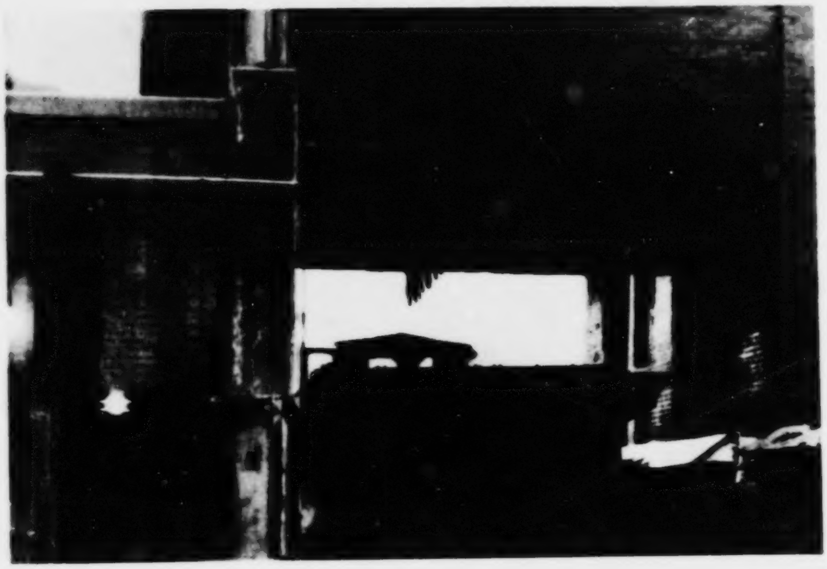


FIGURE 5-7
"WATER ON"

FIGURE 5-8
START OF QUENCH WATER FLOW

FIGURE 5-9
FUGITIVE EMISSIONS A FEW SECONDS
BEFORE THE UP-STACK DRAFT IS WELL ESTABLISHED

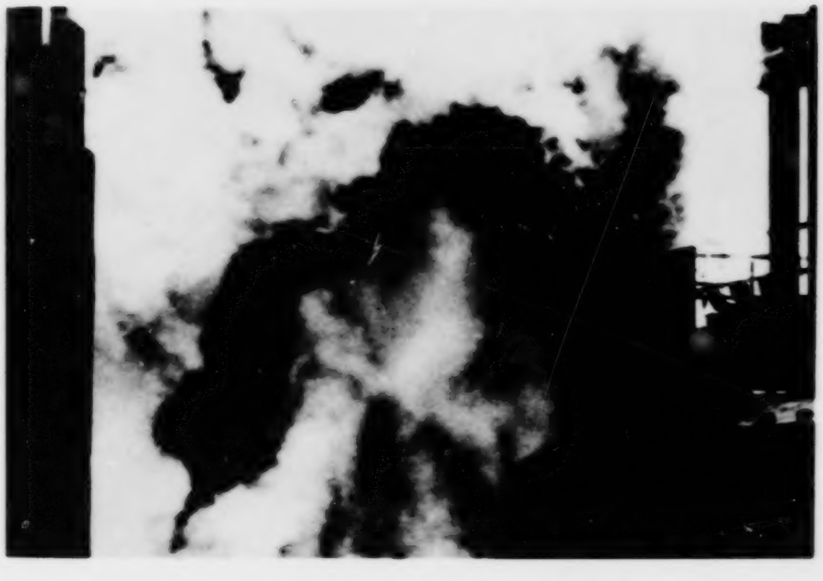


FIGURE 5-10
A VIEW SHOWING THE FIRST ERUPTION OF STEAM

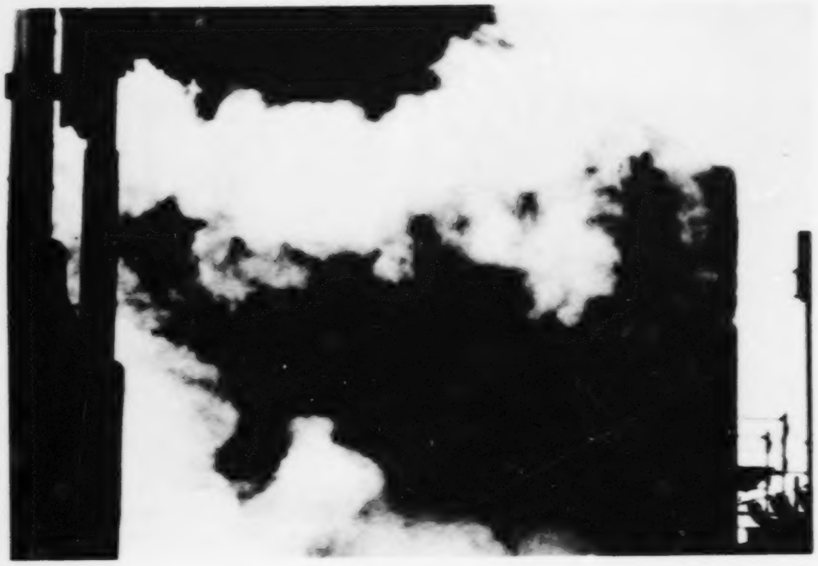


FIGURE 5-11
ANOTHER VIEW SHOWING THE FIRST ERUPTION OF STEAM

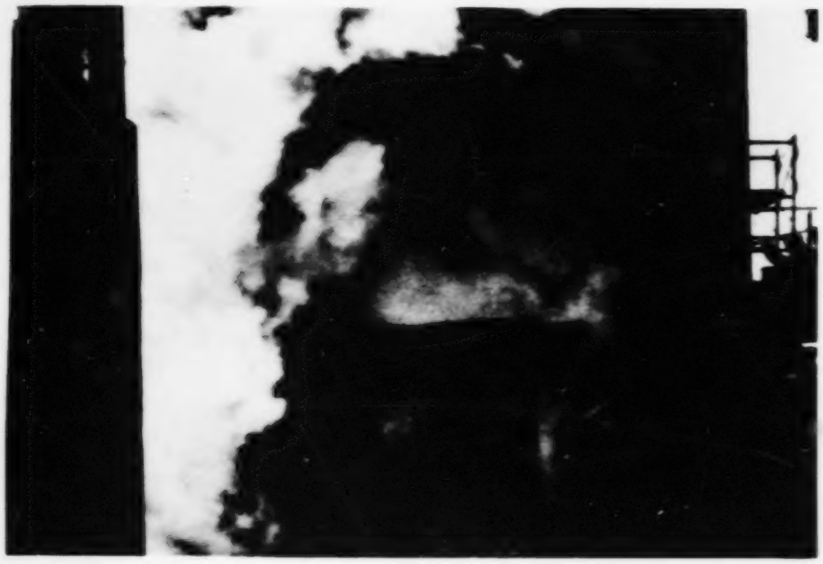


FIGURE 5-12
QUENCH TOWER PLUME

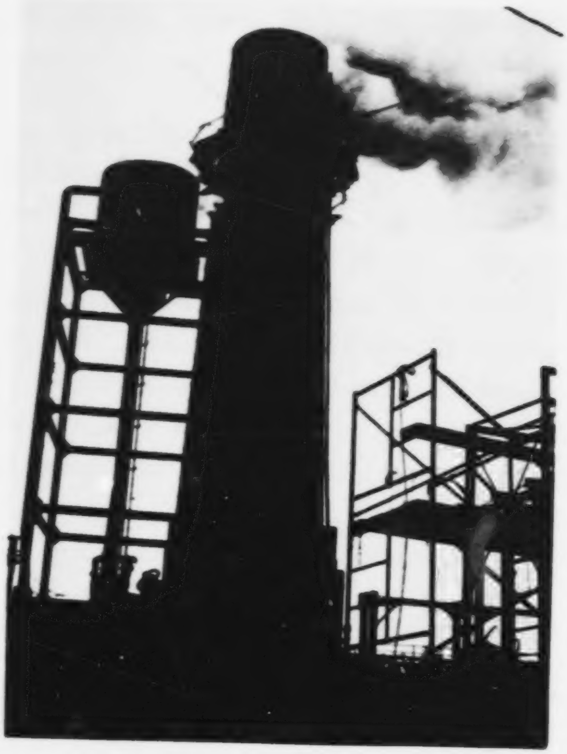
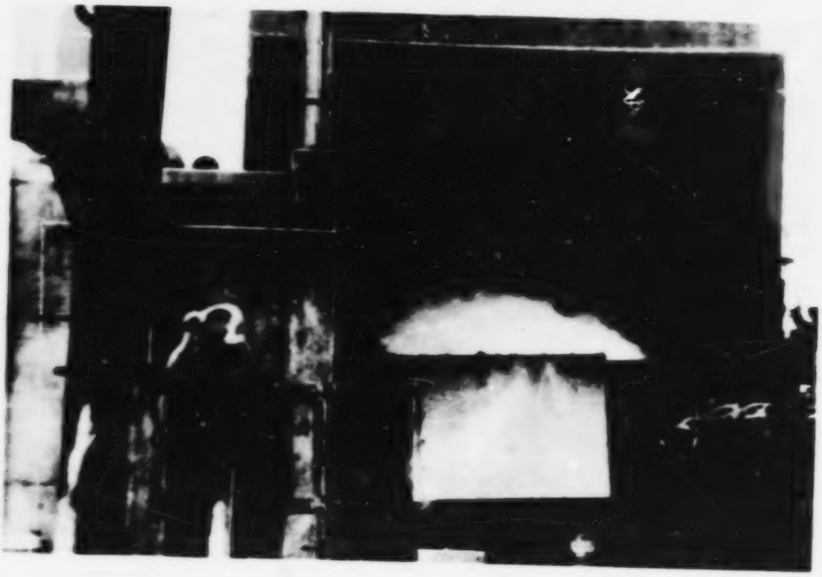


FIGURE 5-13
THE STACK FLOW WELL ESTABLISHED
ABOUT 10 SECONDS AFTER "WATER ON"



and coke particles upwards so that it can be partially removed from the immediate working area, and so that as much of the cooling water as possible may be recovered.

A small amount of water is mechanically entrained as droplets and carried upward by the jets of steam and air leaving the car. Most of the large droplets are eliminated by a single row of baffles. In 1976 it was concluded that the baffles in the quench tower at Lorain had no significant effect on water droplets below about 40 micrometers, nor on particulate matter below about 30 micrometers. The average size of the aerosol which passed through the baffles and exited the stack was about 3 micrometers. In 1977, 10% of the tower cross section was unbaffled open area. Apparently, more of the wooden baffles had burned out because only 6% was unbaffled in 1976.

About four percent of the total water flow continues up the stack as droplets, unhindered by baffles. The balance of the water drains from the car and returns to a storage sump. The sump is designed to collect the quench water for re-use, while allowing the settling of coke particles. This settling action results in a layer of coke sediment in the bottom of the sump. This sediment is cleaned out and hauled away whenever a truck load or two accumulates.

In addition to the physical processes of evaporation, and the cooling and fracturing of the coke, chemical reactions are also ongoing. For example, the coke and water react in the reducing atmosphere to form hydrogen and carbon monoxide. Some of the other components of the quench water (such as ammonia) dissociate to form hydrogen. Additionally, certain components of the quench water, including ammonia, phenol, and cyanide, evaporate from the sump. These substances are also found in the stack gases.(1)

The cooled coke is dumped on an inclined area, called the wharf, which feeds a conveyor belt where it is transferred for storage and eventual use in the steel making process.

During normal operation, quench towers No. 1 and 2 are used for G, H, and I batteries; towers No. 3 and 4 are used for J, K, and L batteries; and tower No. 5 is used for D battery. The hot coke is taken to the nearest tower, with a quench occurring every 10-12 minutes (16-18 minutes in the case of D battery).

All testing was performed on quench tower No. 1. This tower was used only for quenching the pushes from G battery because H battery was being rebuilt and construction blocked the quench car tracks at the G & H boundary.

The operation of the coke ovens at Lorain appears to be typical of the industry so far as operating temperature, coking time, and oven size are concerned. Quench tower emissions would also be expected to be typical, except for the factors of inefficient baffles (already described) and coke greenness. YRC has no broad data base to use for comparing the number of green pushes and is not aware of any such study having been previously made.

6.0 TEST PROCEDURES

6.1 Test Program

The test site was the number one quench tower at Lorain, described in Figure 6-1. The plan of the area around the quench tower is shown in Figure 6-2.

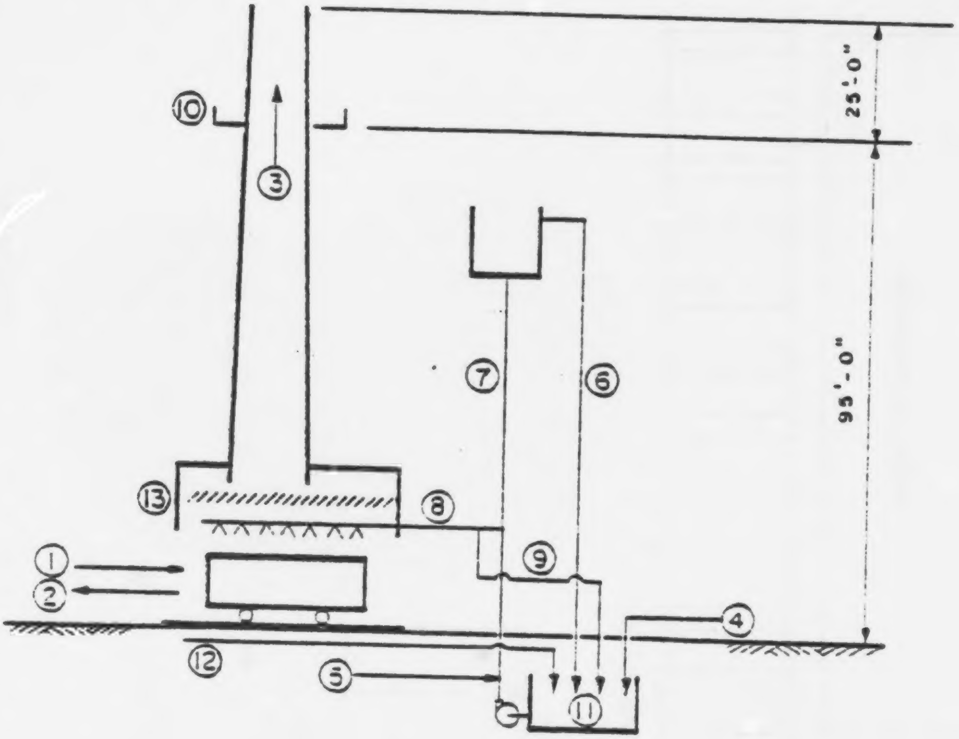
In November 1977, eighteen tests were performed to sample coke quench tower emissions. Emission tests were conducted from a test platform surrounding the tower, 95 feet above the ground (See Figure 6-1.) The operation of quench tower No. 1 and the coke ovens using it presented much the same sampling situation as experienced at that tower in the 1976 tests. Therefore, planned sampling train modifications enabled isokinetic sampling.

The quench tower was placed on clean water and the sump dredged. Conductivity measurements were taken as follows:

October 27	1400 micromhos/cm
October 28	1100 micromhos/cm
October 30	980 micromhos/cm

These measurements are close to those of 855 micromhos/cm and 1450 micromhos/cm for clean sumps in 1976. Although conductivity has no direct relationship to organics in the water, it indicates here whether flushing liquor (containing much dissolved solids and organics)(1) or river water was present. Thus, clean quench water was in use for the tests beginning November 3, 1977. Later, on November 10, 1977, the makeup water was switched to flushing liquor. After five days conductivity measurements showed the sump water to be at the same level of contamination as in the 1976 contaminated water tests, and testing was resumed.

The other process condition, coke greenness, was determined for each quench tested. When the oven doors are opened and the coke is pushed into the waiting car there is a glow from the incandescent coke and varying amounts of flame. If the volatile matter has been completely removed there will be very little smoke

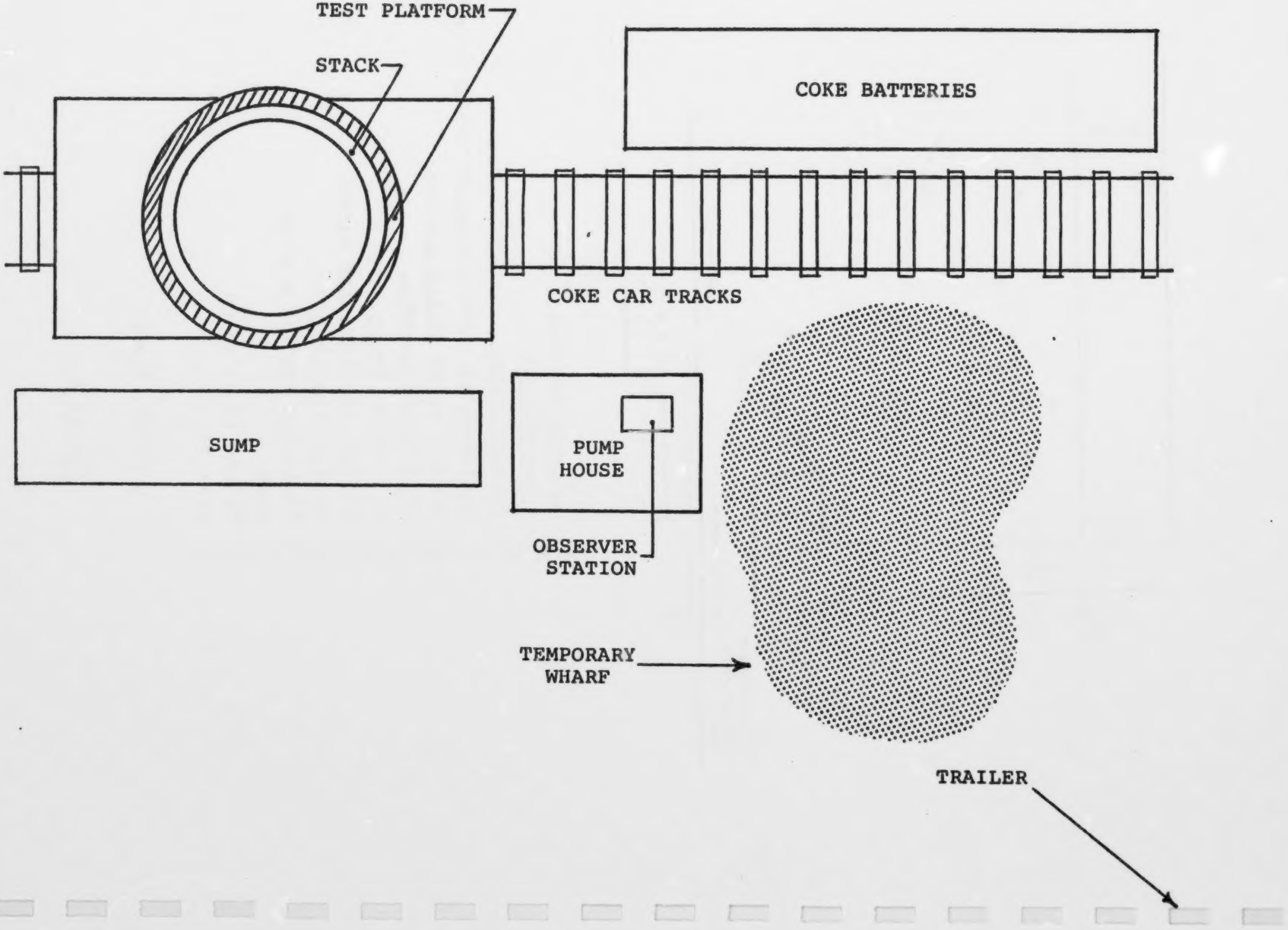


① INCANDESCENT COKE
② QUENCHED COKE
③ EXHAUST GASES
④ CONTAMINATED WATER (FLUSHING LIQUOR MAKE-UP)
⑤ SERVICE WATER (CLEAN MAKE-UP)
⑥ HEAD TANK - OVERFLOW
⑦ HEAD TANK - STAND PIPE
⑧ NOZZLE HEADER (INLET WATER)
⑨ NOZZLE HEADER DRAIN
⑩ EMISSIONS TESTING STATION
⑪ SUMP
⑫ RETURN DRAIN DITCH
⑬ BAFFLES

Quench Tower

FIGURE 6-1

Figure 6-2


TEST PLATFORM
STACK
COKE BATTERIES
COKE CAR TRACKS
SUMP
PUMP HOUSE
OBSERVER STATION
TEMPORARY WHARF
TRAILER

(nongreen coke). Occasionally, however, some of the volatile matter may not be distilled from the coal during the coking process. As a result quantities of gray or black smoke may arise from the coke as it is pushed from the oven. As the car is moved towards the quench tower changing amounts of these dark colored volatile materials arise from certain sections of the car (green coke). On such occasions, after the car is in the quench tower there is a discoloration of the heated air exiting from the stack before the steam plume starts. Each quench car was rated by two observers stationed on the pumphouse roof (see Figure 6-2) just before the car entered the quench tower.

The density of the smoke and the area of the coke's surface emitting smoke were both visually evaluated in accordance with an arbitrary scale from 0 to 5. A rating of 5 designated a very smoky push usually with flames and a rating of 0 designated no smoke and no flames. A reading of 0, 1, or 2 indicated nongreen coke and one of 3, 4, or 5 indicated green coke. The pushes that became part of one test were either all green or all nongreen. If there was disagreement between the observers as far as green or nongreen ratings, the push was not tested.

A series of coke oven pushes were photographed to provide documentation of the coke greenness rating system. Table 6-1 presents the data recorded for these photographs and is an example of the data recorded on coke greenness for each emission test. In addition, photographs of coke greenness in Figures 6-3 to 6-6 give examples of greenness ratings of 0, 2, 3, and 4. This rating procedure was also used in the 1976 study at Lorain and resulted in very consistent ratings for the several observers.(1)

A summary of the quench tower emission tests and corresponding process conditions of water quality and coke quality is presented in Table 6-2.

TABLE 6-1

INDEX OF PHOTOGRAPHIC SLIDE NUMBER AND OBSERVERS GREENNESS RATING AND COMMENTS ON A SERIES OF PUSHES

Photographic slide number	Push No.	Oven No.	Greenness (Note)		Coke Level	Flames	Smoke Color
1-2-3	1 NT*	24	4	4	High	Yes	dark gray
4-5	2 NT	34	3	3	High	Yes	dark gray
6-7	3 NT	44	1	2	High	No	gray
8-9-10							
11-12	4 NT	54	1	2	High	Yes	gray
13-14-15							
16-17	5 NT	64	2	2	High	Yes	light gray
18-19-20	6 NT	6	3	3	Very High	Yes	dark gray
21-22-23	1 V	26	4	4	High	Yes	dark gray
NA	2 NT	36					
NA	3 T	46					
NA	4 T	56					
24-25-26	5 NT	8	4	4	High	Yes	dark gray
27-28	6 T	18	0	0	High	Yes	light gray
29-30-31-32	7 NT	28	4	4	High	Yes	black
NA	1 T	38					
NA	2 T	48					
NA	3 NT	58					
33-34	4 T	1	2	2	High	Yes	light gray
35-36-37-38	5 T	11	2	2	High	No	gray
39-40-41	1 NT	21	1	1	High	No	light gray
42-43	2 NT	31	3	3	High	No	gray
44-45-46	3 NT	41	1	1	High	Yes	light gray
47-48	4 NT	45	1	0	High	Yes	light gray
49-50	5 NT	51	3	3	High	Yes	gray
51-52	6 NT	61	2	2	High	Yes	gray
53-54	7 NT	3	0	0	High	Yes	light gray

Note: Two observers rated the greenness of the car
All pushes were from G battery.

PHOTOGRAPHS ILLUSTRATING COKE GREENNESS RATINGS

FIGURE 6-3

OVEN 3 PUSH 7 GREENNESS RATING OF 0

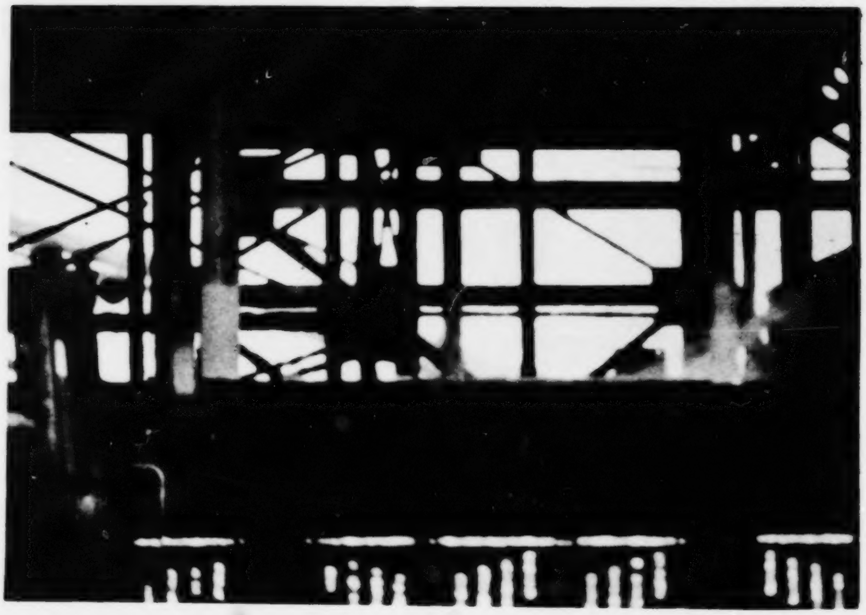
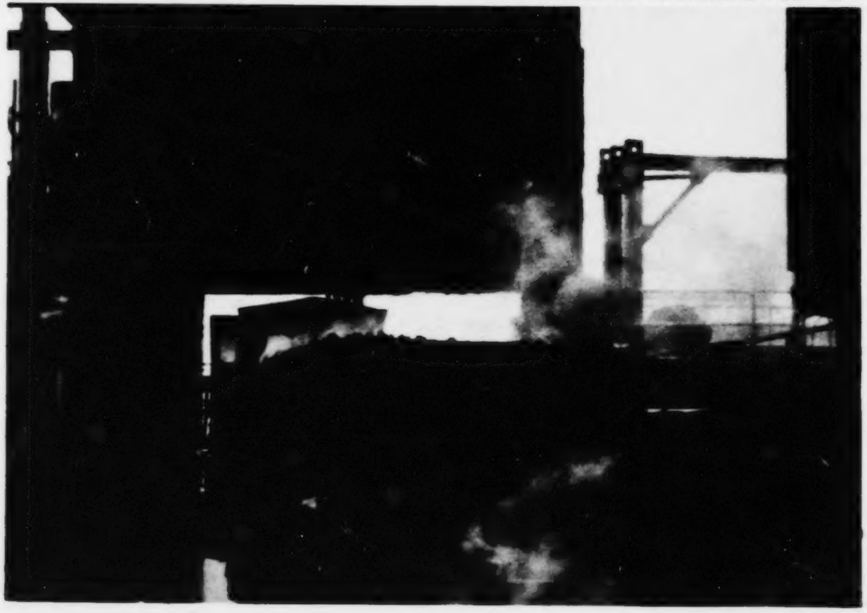


FIGURE 6-4

OVEN 1 PUSH 4 GREENNESS RATING OF 2



PHOTOGRAPHS ILLUSTRATING COKE GREENNESS RATINGS

FIGURE 6-5

OVEN 34 PUSH 2 GREENNESS RATING OF 3

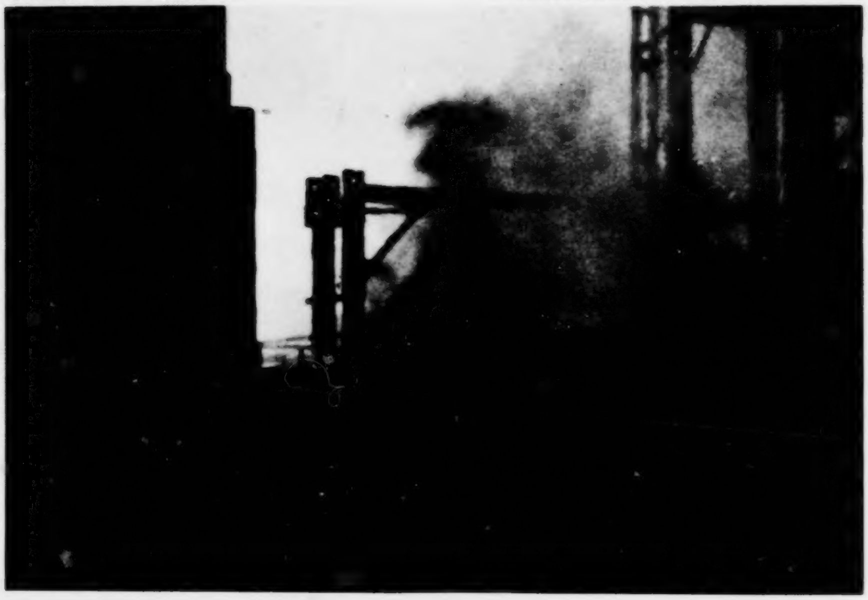


FIGURE 6-6

OVEN 28-3 PUSH 7 GREENNESS RATING OF 4

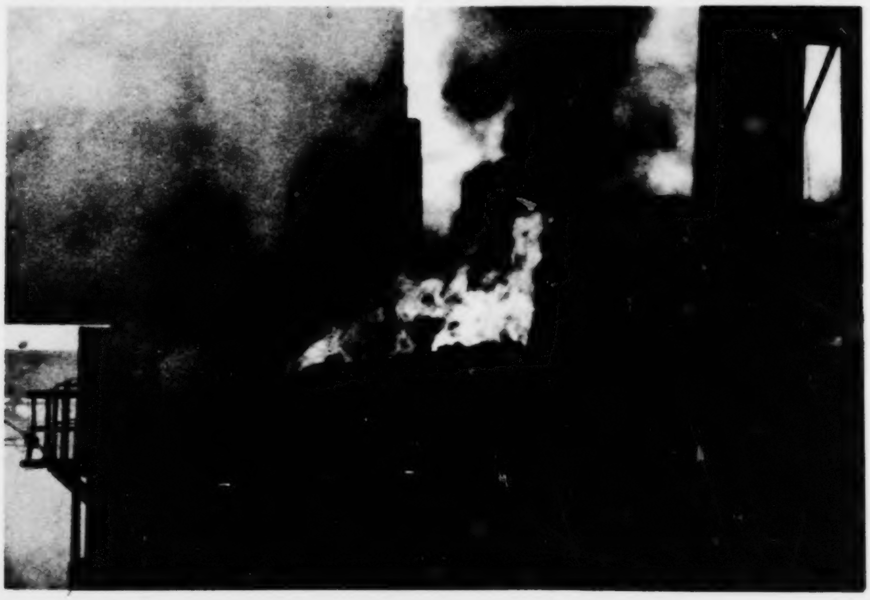


TABLE 6-2

COKE QUENCH TOWER EMISSIONS TESTS

Clean Quench Water

Date	Test Type and No.	Average Greenness Rating	Coke Greenness[a]
11/3/77	1 Benzene soluble	3.0	G
11/4/77	2 Benzene soluble	1.8	NG
11/5/77	2B Organic emissions	3.4	G
11/5/77	3 Organic emissions	3.3	G
11/6/77	4 Organic emissions	1.6	NG
11/7/77	5 Organic emissions	4.0	G
11/7/77	6 Organic emissions	1.6	NG
11/8/77	7 Organic emissions	1.2	NG
11/8/77	8 Organic emissions	1.8	NG
11/8/77	9 Organic emissions	1.6	NG
11/8/77	10 Organic emissions	1.5	NG
11/9/77	11 Organic emissions	3.2	G
11/9/77	12 Organic emissions	3.7	G
11/9/77	Biological test		

Contaminated Quench Water

Date	Test Type and No.	Average Greenness Rating	Coke Greenness[a]
11/15/77	13 Benzene soluble	1.5	NG
11/16/77	14 Organic emissions	1.5	NG
11/19/77	15 Organic emissions	0.5	NG
11/19/77	16 Organic emissions	0.3	NG
11/19/77	17 Organic emissions	0.5	NG
11/19/77	18 Organic emissions		-

[a] NG = Nongreen (0-2 greeness rating); G = Green (3-5 greenness rating)

The various parameters measured concurrent with the emission tests are identified in Table 6-3, along with measurement and analytical methods, and sampling location. Samples of quench water were taken on November 9th, 16th, and 19th from the clean water makeup and inlet (positions 5 and 7 on Figure 6-1) and from the contaminated water makeup and inlet (positions 4 and 7). Water flow rates to the quench process were not measured but were assumed to be the same as in the 1976 tests. An examination of the pumping and piping system revealed no significant change and supported such an assumption.

6.2 Sampling Problems

Previous test techniques and methods used in attempts to characterize air pollution emissions from quench towers were often plagued with difficulties. These included the exclusion of certain size ranges of particulate matter in particulate measurements and limitations in obtaining measurements of important process parameters. Early attempts at particle measurement using greased plates(2) and petri dishes(3) succeeded in measuring only large diameter, heavy droplet and/or solid particles. Further attempts by State and local agencies to measure particulate emissions utilizing standard EPA sampling equipment were limited in their scope and also encountered a number of sampling difficulties.(4,5)

Major problems occurred because, in operation, the quench tower generated short violent rushes of steam which hampered efforts to accurately read and adjust the sampling instrumentation to maintain isokinetic conditions. In this case, the EPA guidelines were not usable because they recommended measuring velocities and making adjustments every 3 to 5 minutes. This time interval was more than the total duration of a quench. The short duration of the quenches made capturing the prescribed volume of gases difficult. The square shape of most quench towers, and the use of internal partitions compounded these problems by causing uneven flows across the tower cross-section. In addition to

TABLE 6-3 SUMMARY OF MEASUREMENTS-COKE QUENCH TOWER EMISSION TESTS

Measured Parameter	No. of Tests	Measurement Method	Analytical Method	Sampling Location (Figure 6-1)
Organic matter loading 95 clean water quenches 19 contaminated water quenches	15	EPA 5 Modified with porous polymer resin (XAD-2)	IR, LRMS Combined gas chromotography/ mass spectrometry	(10)
Benzene soluble matter (26 quenches)	3	EPA 5 Modified	EPA 5 Modified	(10)
Mutagenicity and cytotoxicity	1	Hi Vol sample using modified EPA 5 train	Ames Mutagenicity Assay Clonal Cytotoxicity Assay	(10)
Gaseous Hydrocarbons (Benzene and THC)	2	Grab sample	Gas Chromatograph	
Particulate	17	Component of modified EPA 5 train	Weight collected	(10)
Size Distribution: Particulate	17	20 μm cyclone	Weight collected	(10)
Water Quality Total solids Total organic carbon	29	Composite samples taken from lines or from sump	EPA Methods for Chemical Analysis of water and wastes	Flushing Liquor (4) Service water (5) Inlet (7) Sump
Greenness of coke	140	Visible Observation (photo and movies)		Pump house roof (8)
Oven coking time	140	Plant data		
Oven Heat temperature	140	Plant data		

the above problems, droplets in the exhaust stream plugged filters, and made determinations of the molecular weight of the gases nearly impossible.

Potential problems that had existed during earlier testing attempts were overcome in 1976 by an extensive planning period in which previous tests were scrutinized, test equipment was researched, and engineering judgments were made as to the most effective methods available for conducting the tests. In 1977, the use of special equipment such as the organic adsorber unit required further modification to the EPA Method 5 train.

Table 6-4 lists the major problems, their possible effects on test accuracy, and the solutions that were utilized to overcome these problems.

6.3 Sampling Equipment Design

Organic Characterization Sampling Train (OCST)

To determine organic emission rates, tests were conducted using a high volume sampling train with an organic adsorbent unit (Figure 6-7). This was equipment frequently used for EPA Method 5 but modified as described below.

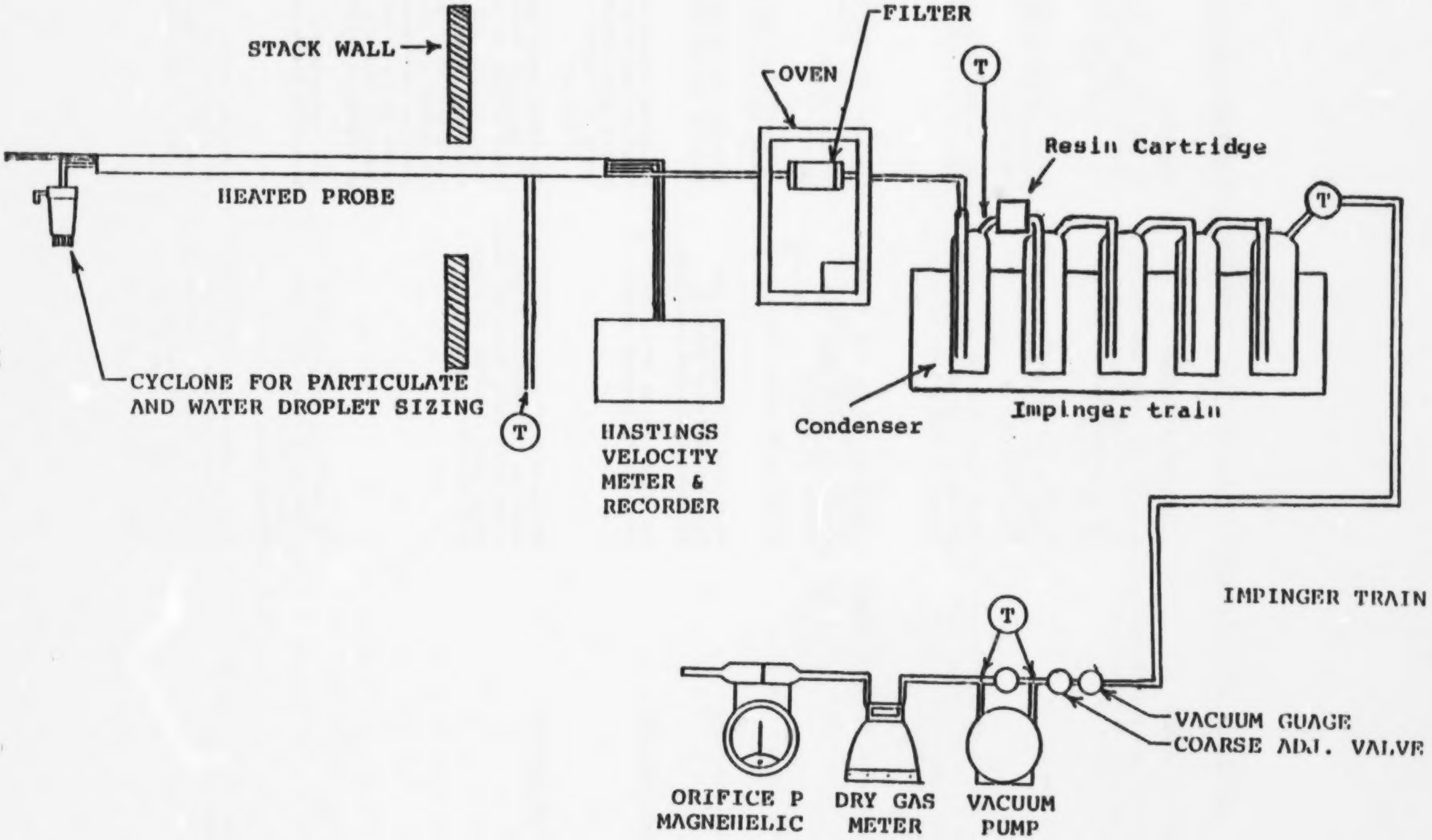
A button hook sample nozzle of stainless steel (SS) was connected by (SS) swagelock fittings to a special cyclone. This cyclone was constructed of (SS) and was designed to have a 50% cut size of approximately 20 micrometers at the flow rates used in the tests. The 50% cut size (or D_{50}) designates the size at which the collection efficiency is 50 percent - where half the particles encountered are captured and half escape. The cup of the cyclone was fitted with a Viton gasket. The cyclone was connected to the probe with (SS) swagelock fittings.

The 10 foot (SS) probe was heated to 250°F. The probe was connected with (SS) swagelock fittings to a filter holder. The filter holder was made of (SS) and coated inside with Teflon.

TABLE 6-4 POTENTIAL PROBLEMS AND SOLUTIONS IN TESTING QUENCH TOWER EMISSIONS

Potential Problems	Effect on Accuracy	Solution
Anticipated small differential in TDS between clean and contaminated quench water.	A wide TDS range desired to show effects on clean and contaminated quench water on emissions.	At Lorain, the ratio of contaminated water TDS to clean water TDS was on the order of 10:1.
Tower Configuration	Square, squat, sectionalized towers likely to produce non-uniform flow.	Tall circular tower with no internal buttressing was selected.
Short duration of quench resulting in velocity profiles changing faster than can be measured or recorded by usual methods.	Velocities move up and down so rapidly as to make accuracy difficult to achieve.	Use of Hastings-Raydist velocity meter with continuous recording.
Water droplets in stack sample	Inability to measure actual moisture content, molecular weight of stack gas, and filter plugging.	Cyclone (50% cut size about 20 microns) was fitted to the front of the probe.
Droplets and grit in stack gases	Plugging of pitot tubes	Used Hastings Raydist velocity meter with continuous purge.
Fugitive emissions	Emissions exiting from entrances of tower causing non-representative sampling.	Entrance emissions monitored and testing halted when excessive.
Sampling locations	Possible uneven velocity patterns throughout stack.	Performed traverse of 12 points velocity and selected position B1 for coke quench tower emission tests (18 tests).
Number of quenches	EPA Method 5 would require sampling 20 quenches to get a one hour test, however, this would have resulted in plugging and other errors.	The 1976 tests showed that four (4) quenches would provide sufficient weight of particulate (over 100 mg) and volumes of dry stack gas (over 15 cubic ft.) using a high volume sampler for EPA Method 5. However, additional quenches were tested in 1977 because of the lower sample rates required when the train included an organic adsorbent unit.
Skewed flow	The vertical component of velocity differs from the linear velocity along a skewed flow.	Vane measurements were made to determine probe positioning.
Greenness of car varies from push to push.	Unless greenness can be characterized for each car its effect on organic loading in the quench effluent might negate any attempt to determine origin(s) of organics.	A rating system (developed in 1976) was expanded and movies and photos were taken to document a typical series of observations.

Figure 6-7
ORGANIC MATTER AND PARTICULATE SAMPLING TRAIN
USING MODIFIED EPA METHOD FIVE


STACK WALL
FILTER
OVEN
Resin Cartridge
T
T
HEATED PROBE
CYCLONE FOR PARTICULATE
AND WATER DROPLET SIZING
T
HASTINGS
VELOCITY
METER &
RECORDER
Condenser
Impinger train
IMPINGER TRAIN
T
VACUUM GUAGE
COARSE ADJ. VALVE
ORIFICE P
MAGNEHELIC
DRY GAS
METER
VACUUM
PUMP

Viton and Teflon gaskets were used to seal the two halves of the filter holder. Spectrograde Type AE glass fiber filters with an efficiency of 99.99% for particles larger than 0.3 micrometers were used. A (SS) braided line connected the filter holder to a (SS) female impinger connector. This connector was greased with silicone and placed into a glass impinger. The glass impinger was in an ice bath where it was cooled to approximately 68°F. Water and some organic material were recovered in this condenser. The adsorbent cartridge located after the condenser employed a porous polymer resin (XAD-2) contained in a tube sealed at top and bottom. The unit contained approximately 32 grams of XAD-2. A thermocouple was placed in the inlet (SS) fitting to the adsorber to monitor the temperature. The outlet fitting (glass) from the adsorber was connected to a standard Lexan impinger unit. Two of these impingers contained 250 ml of water, the third was empty and the fourth contained 350 grams silica gel. Viton gaskets and small amounts of silicone grease were used to form a vacuum proof seal on the impingers. The use of silicone grease in this location would not interfere with samples collected since the impingers are downstream of all samples taken. However, the silicone grease used on the condenser might introduce this substance to the samples.

Velocity pressure (Δ p) was measured with a Hastings-Raydist meter which operates as follows. A continuous strip chart recorder was connected to a Hastings meter to record the velocity head pressure (Δ p), and to aid in verifying any uneven flow patterns. Purge gas (air) was injected into a pneumatic bridge arrangement formed by the velocity transducer, manifold and pitot tube. At zero velocity, the bridge was balanced so that no flow occurred through the velocity transducer and purge gas exhausted equally through both openings of the pitot tube.

As flow across the tip occurred, a differential pressure was developed, unbalancing the bridge and causing a small amount of purge gas to flow through the transducer. The transducer measured the flow which was related to the main gas flow at the tip of the pitot tube. Purge gas still exhausted through both openings, but at slightly unequal rates.

The purge gas continually exhausted into the stack, thereby preventing water and large particles from plugging the pitot lines. This instrument allowed accurate measurement of flow even though high particulate concentrations were present.

Benzene Soluble Sampling Train (BSST)

The train configuration, all train components, and sampling methods were the same as those described for the OCST, except for the sample recovery phase.

Biological Sampling Train (BST)

The primary function of this train was to collect a large sample of gaseous emissions. This "hi-vol" sample was collected specifically for mutagenicity and cytotoxicity tests. This sampling train was also identical to the OCST, except for the sample recovery phase.

6.4 Sampling Technique

In November 1977 several tests were performed prior to beginning the full field test. Velocity profiles were obtained for 12 points. These preliminary profiles were analyzed for each one second time interval for magnitude of Δp. The Δp's of each interval were then added together and averaged by dividing the time of each quench into the total. Visual comparison of overlaid profiles showed that roughly the same pattern, time and velocity heads were found for each quench, suggesting that velocity heads for a particular point in the stack could be predicted, and these 1977 profiles were similar to those obtained in the 1976 tests.

Analysis of the above preliminary velocity work indicated that isokinetic sampling conditions could be maintained throughout the quench process by running a velocity test during the first quench in a series. This test could be quickly analyzed and graphed as velocity versus elapsed time. Data from the velocity profile were then utilized to determine:

- Velocity Pressure (Δ p)
- Velocity (feet per minute)
- Required nozzle size
- Predicted sampling rates

If the preliminary test indicated the presence of an erratic flow pattern, the test was delayed until a predictable flow was established. If stack flows were predictable, testing could be continued and the sampling rates would constantly be adjusted based upon the graph. Thus, the sampling flow rate would increase and decrease coincidentally with the tower's exhaust flow rate. This type of graphical analysis is illustrated in Figure 6-8. It will be noted that three sections of the profile can be defined, namely:

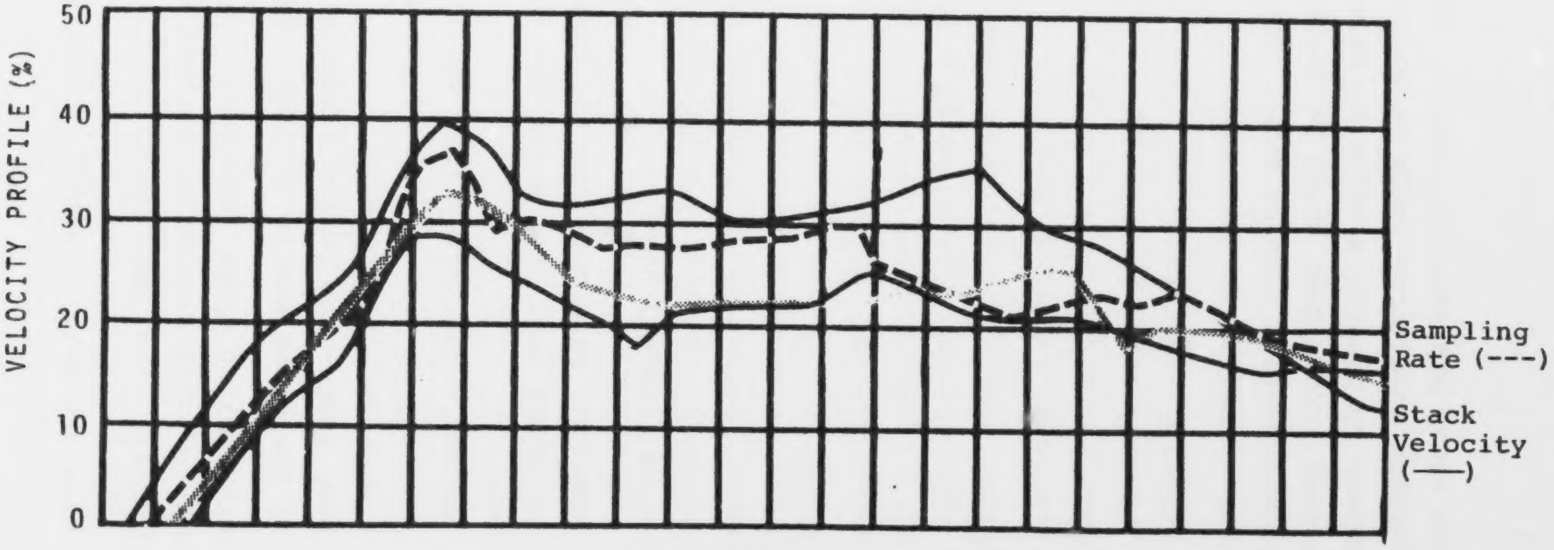
- Ramp Up - From the time the coke car entered the tower until the water hit the incandescent coke.
- Plateau - The time during which the plume velocity is either flat or gently rising to a peak and then holding.
- Ramp Down - The period during which the velocity of the plume starts to fall rapidly.

In order to set sampling rates from these Δ p's, velocity equations were computed utilizing data obtained from the particulate sampling in October, 1976, consisting of:

- Moisture data obtained in accordance with EPA Method 4.
- Orsat samples obtained in accordance with EPA Method 3 with the use of two condenser units to trap entrained water droplets.

FIGURE 6-8

VELOCITY PROFILE



10 SECONDS/CM

The Velocity Profile (%) represents the scale of the Hastings flow meter. Full scale on this meter is 50%; the % readings correspond to velocity head pressures (Δp) measured in inches of water. The conversion to Δp is dependent upon the pre-calibration range determined for the Hastings meter.

These data were verified during the first 1977 tests. In addition to the velocity traverses, initial measurements were performed to determine the maximum angle of flow in the tower. Data from these findings along with the 1976 data indicated that sampling should be conducted near 110 degrees measured from the horizontal.

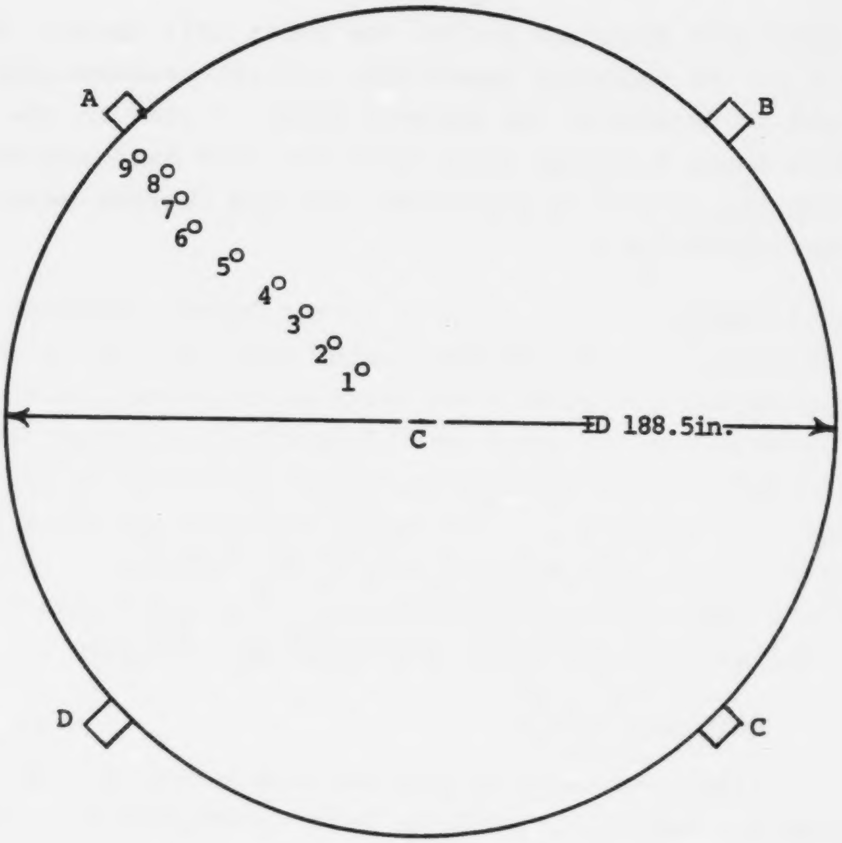
The requirements for the organic matter tests suggested that both the clean and contaminated water tests including the green coke versus the non-green coke tests be conducted at one point. Based on this preliminary test information and after reviewing the 1976 data it was decided to perform the organic matter tests at point B1 (Figure 6-9). In order to assure as large a sample as possible each test sampled four to six quenches. In order to reflect the total quench emissions, sampling began when the quench car entered the tower and ended when it left.

6.5 Test Sequence

Since velocity results were reproducible within a time frame of approximately one hour, profiles were taken preceding each test run to determine sampling rates for the test. Sampling rates for an average test profile are shown in Figure 6-8. The problem was to maintain the correct sampling rate (ΔH) over the entire quench period (from car-in to car-out), allowing for the rise and fall of both the velocity head (Δp) and the stack temperature. For each quench test the sampling rate (ΔH) was gradually increased from the signal car-in to approximately 0.50 inches of water over a thirty second period. This maximum sampling rate was maintained until the signal water-off was given and a ramp-down procedure was initiated to a pre-determined rate (approximately 0.25 inches of water) which was established by averaging the ramp-down portion of the velocity profile. Sampling was terminated when the car was completely out of the tower.

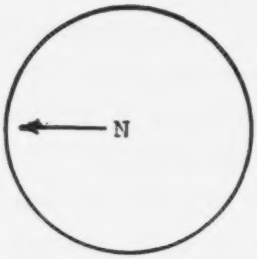
FIGURE 6-9

SAMPLE POINT LOCATION



A
B
9
8
7
6
5
4
3
2
1
C
D 188.5in.
D
C

Pt.No.	Inches from stack wall
1	71.60
2	55.60
3	44.40
4	35.40
5	27.50
6	20.50
7	14.10
8	8.25
9	2.65
C	94.25



If a major velocity variation occurred during sampling, (10-20% change from velocity profile) a new sampling rate was determined and implemented within 5-10 seconds.

The area under the profile curve was not used to determine sample rates required during field tests. Instead, 6-second blocks were averaged to establish the Δp readings and, in turn, the necessary isokinetic sampling rates (ΔH). The averaging method was used to reduce calculation time since a field computer was not available.

The techniques applied to measurement and plotting of velocity profiles assured that 13 of the 17 tests were within the required range for standard EPA Method 5 (± 10 percent of 100 percent isokinetic). The tests listed below were not within this range:

TABLE 6-5

Test Number	Below 100%	Above 100%
9		138
11	86	
14	70	
17	89	

Individual stack flows for the tests varied by 17% more than the average and 11% less than the average. These variations and the variation from quench to quench may have been due to differences in:

- Moisture content of the stack gas
- Probe position
- Wind speed and direction
- Total tonnage of coke quenched
- Coke temperature

Test results are included in Appendix A. Once a successful velocity profile had been run, 4 to 6 subsequent quenches were sampled to make a test. The normal test sequence went as follows:

Incandescent coke was pushed from an oven into a quench car which was driven down the tracks to quench tower No. 1. The two observers on the pump house roof recorded their ratings of coke greenness and if the ratings disagreed between green and nongreen, no sampling would be performed on that quench.

When the coke car entered the tower the observers notified the sampling crew and the test began. When quench water began to spray from the nozzles the signal "water on" was given.

Fugitive emissions began to escape from the bottom of the tower. During a period of approximately 25 seconds immediately after the quench water started flowing there was more steam generated than could be drafted up the tower. See Figures 6-10 and 6-11. Frequency and duration of fugitive emissions from the eastern opening of the quench tower were noted by one of the observers. The quantity of steam involved in the fugitive emissions was difficult to judge, but if the total fugitive emissions from both portals was deemed excessive, the test was cancelled by the project director. The fugitive emissions averaged 17% of the total sample time as shown in Table 6-6.

The proper adjustments were made in the sampling rate from the previous signal of car in to water off and car out. The total sampling time was recorded by instrumentation installed in the field trailer.

6.6 Coke Quench Tower Emission Tests

During several of the test runs with clean quench water, holes were found in the center of the filters. It was concluded in the 1976 test report(1) that particulate matter caught on the filter would be smaller than 5 µm, ranging downward toward submicron sizes. During the clean water tests, there was a relatively small quantity of particulate matter retained on the intact portion of the filter, while during the contaminated water

FIGURE 6-10
FUGITIVE EMISSIONS AT START OF QUENCH

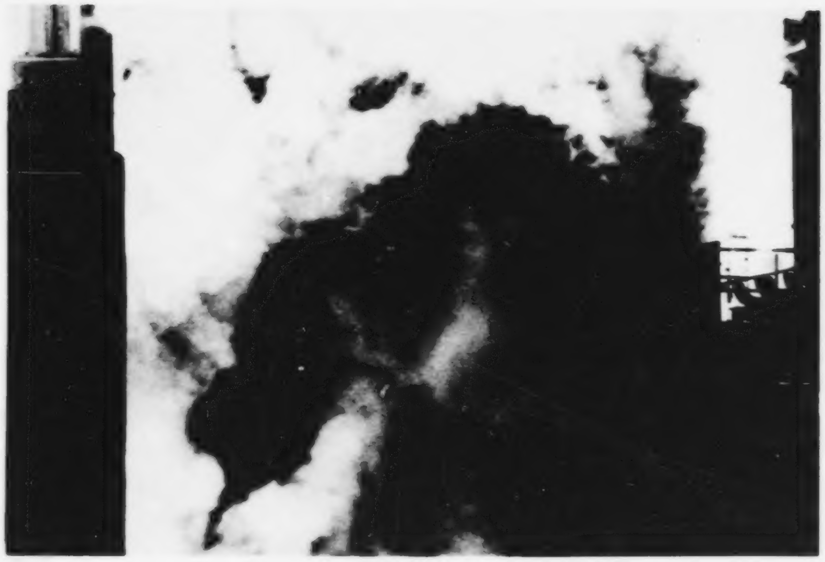


FIGURE 6-11
FUGITIVE EMISSIONS A FEW SECONDS AFTER
BEGINNING OF QUENCH

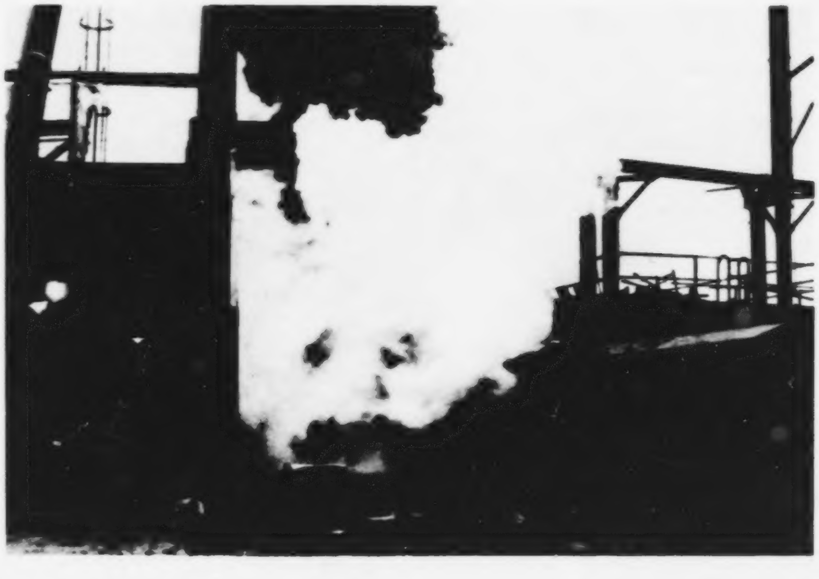


TABLE 6-6

FUGITIVE EMISSIONS

Test Number	Fugitive Duration (Sec.)	Sampling Duration (Min.)
1	15	2.4
1	13	2.3
1	7	2.8
1	10	2.4
1	19	2.4
2	29	2.7
2	40	3.1
2	25	2.7
2	42	3.0
2	37	2.8
2B	15	2.6
2B	16	2.3
2B	19	2.4
2B	13	2.4
2B	15	2.3
3	15	2.4
3	13	2.3
3	16	2.4
3	15	2.3
3	16	2.2
4	22	2.5
4	36	2.3
4	18	2.4
4	17	2.4
4	20	2.4
5	22	2.5
5	21	2.6
5	25	2.4
5	38	2.4
5	29	3.0
6	17	2.3
6	21	2.4
6	17	2.4
6	15	2.4
6	33	2.4
7	18	2.4
7	30	2.4
7	38	2.4
7	17	2.5
7	16	2.5
8	22	2.3
8	19	2.3
8	17	2.4
8	20	2.4
9	NA	2.0*
9	12	2.5
9	20	2.7
9	27	2.4
9	27	2.5
10	25	2.3
10	20	2.4
10	15	2.3
10	21	2.5
11	18	2.4
11	NA	2.6*
11	7	2.7
11	25	2.4
12	7	2.7
12	11	3.3
12	27	2.2
13	27	2.4
13	15	2.7
13	25	2.4
13	26	2.4
13	20	2.4
13	19	2.4
14	61	2.4
14	40	2.6
14	55	3.7
14	125	2.4
14	55	2.5
15	58	2.4
15	51	2.4
15	44	2.5
15	39	2.4
16	51	2.4
16	44	2.4
16	39	2.5
16	20	2.4
17	23	2.6
17	38	2.4
17	25	3.0
17	22	2.6
17	26	2.5
17	27	2.7
	2175	208.0

Fugitive Duration ÷ Sampling Duration x 100 = 17%

* Not included in total

tests, a larger quantity was caught. This larger quantity of particulate matter may have been initially deposited on the filter directly in front of its inlet, thus protecting this area from the continuing abrasive action of particles smaller than 0.3 µm as they passed through the filter. Test work conducted by YRC at Research Triangle Park(6) for EPA involving wind tunnel tests with low grain loadings and small diameter particles produced much the same effect. Redesign of the inlet to the filter should be considered so as to reduce the velocity of the incoming particles and to disperse them over a larger area of the filter.

6.7 Sample Recovery

Sample recovery was performed in two stages. First, each sampling train was partially disassembled and all water catches stoppered at the sampling location. Then, further disassembly and clean-up were performed in the laboratory trailer. All sample recovery procedures were the same for each of the three test types: organics, benzene solubles, and biological tests, except that different solvents were used to wash the train components during clean-up. The washes used were:

Test	Solvent
Organics	Methylene chloride
Benzene soluble	Distilled water then benzene
Biological	Distilled water

At the completion of each test the probe and cyclone assembly was removed from the stack and its exterior wiped clean. The cyclone cup was removed, its contents poured into a clean, labeled container and the cup replaced in the cyclone assembly. The condenser (impinger) was removed and capped. The filter holder, umbilical line, and adsorber-impingers assembly were disconnected and each was capped. After inspection and recording of any anomalies, the individual units were lowered from the test platform and taken to the laboratory trailer for clean-up.

The samples generated from each sampling train during laboratory procedures were:

1. Cyclone catch and wash
2. Probe wash
3. Filter
4. Condenser catch and wash
5. Adsorber unit
6. Solvent blanks

The volumes of the cyclone catch and the condenser catch were recorded. Water caught in the back impingers and in the silica gel was used to determine moisture values for each test. No organic analyses were performed on train components positioned after the adsorber unit.

In the laboratory trailer, clean-up and disassembly of the sampling train were conducted in the following order:

1. The cyclone catch was measured to the nearest milliliter and returned to its container. The inside of the cyclone was cleaned by rinsing with solvent and brushing between each rinse with a precleaned nylon brush. This was continued until the rinse showed no visible particles. The rinses were added to the cyclone catch.
2. The nozzle was carefully removed and the inside surface cleaned in a manner similar to the cyclone until the rinse showed no visible particles. All rinses were added to the probe wash.
3. The probe liner was rinsed by squirting solvent into the upper end, while tilting and rotating it to assure that all inside surfaces were cleaned. The water was drained from the lower end into the sample container. A second rinse using the same procedure was then performed with the aid of a probe brush, which was pushed through the entire

length of the liner using a twisting action. The brushing and rinsing operation was repeated until no particulate matter remained in the probe liner upon visual inspection. Upon completion of the brushing and rinsing operation, the brush was rinsed with solvent and the liner was given a final rinse. These rinsings were collected in a glass jar.

4. The inside of the front half of the filter holder was cleaned by double brushing with a nylon bristle brush and rinsing with solvent until all visible particulate was removed. The brush and the inside surface of the front half of the filter holder were then given a final rinse. All rinses were added to the probe wash.
5. The filter was removed from the holder and was inspected for tears, punctures and other deformations before being placed in a clean glass jar.
6. The volume of the condenser catch (first impinger before adsorber) was measured to the nearest milliliter and the inside of this impinger brushed with a nylon brush and rinsed with solvent. The catch and rinses were poured into a glass jar.
7. The inside of the back half of the filter holder and the inside of the tubing (filter holder to condenser and condenser to adsorber) was cleaned by brushing with a nylon brush and rinsing with solvent. These washes were added to the condenser catch.
8. The adsorber unit was fully disconnected and capped.
9. The liquid in the first three impingers and the condensate from the umbilical cord were measured to the nearest milliliter and recorded. The umbilical cord was washed, this wash was not collected.
10. The silica gel from the last impinger was transferred to a pretared container, weighed to the nearest 0.1 g and recorded.

A blank test was prepared for inclusion in the organic emission test series by additional rinsing of a train with methylene chloride. Upon completion of Test No. 17, the nozzle, cyclone, probe, filter holder, and condenser were rinsed a second time. A third wash was done and saved as the blank. An unused organic adsorber and glass fiber filter were also labeled as part of the blank test.

Each of the five samples generated from the laboratory clean-up (except the adsorber unit) was put in a glass jar. The lids were sealed tightly with teflon tape. All samples were stored under refrigeration and out of sunlight both on-site and during shipment to York Research in Stamford or Arthur D. Little in Boston, for extraction and/or analysis.

6.8 Precision of Sampling Methods and Estimated Probable Error for Analytical Procedures

In order to place a measure of reliability to the data obtained from this program, it is necessary to examine the various processes and measurements carried out in achieving the final numerical result. Once the reliability of each step is assessed, it is then possible to compute the probable error associated with the data point.

Probable error is defined as a plus or minus quantity within which limits the actual accidental error is likely as not to fall. It is an indication of precision and does not signify either the actual error, or the error most likely to occur.

To evaluate quantities derived from field test data, many equations are used in ways that combine one or more measured quantities resulting in determination of such things as the Total Air Emission, Volumetric Flow, and Volume of Sample tested; to mention a few. With each such quantity there exists an associated maximum possible error. When several quantities are combined in some fashion, as in an equation, these errors tend to accumulate and compound themselves. A common procedure for determining the maximum probable error for any combination of quantities is discussed on Page 1, 6, 7 of the Civil Engineer's Handbook,(7) and was used in the following calculations for maximum probable error.

This method is given as follows for calculating the probable error (Es) for related quantities of differing reliabilities:

$$(\text{eq.1})\quad E_s = \sqrt{E_1^2 + E_2^2 + E_3^2 + \ldots\ldots + E_n^2}$$

where E_1 through E_n are the probable errors for the independent quantities.

As an example of the procedure used in calculating the probable error, the following example is given:

$$\text{Air Emission (lb/T.C.)} = \left[\frac{\text{mg}}{V_{m_{std}}}\right] \left[\text{scfm}\right] \left[\text{C}\right]$$

where: mg is the sample weight

$V_{m_{std}}$ is the volume of the sample tested

scfm is the volumetric flow

C is conversion constants $(C_1, C_2, \ldots C_n)$

The first three quantities contain other independent quantities that also have errors associated with them; they too must first be analyzed for maximum probable error in order to determine a maximum probable error for the total Air Emission results.

As a part of the overall calculation, it was necessary to calculate the volume of the sample tested. Maximum errors for each component of the calculation were obtained from a paper by Shigehara, et al.(8)

This sample calculation is shown below in its entirety. It should be noted that dimensions, like conversions, have no bearing on maximum probable error determinations and have not been included.

$$V_{mstd} = (C_1) \left[\frac{V_m \quad (P_b + \frac{P_m}{C_2}}{(T_m + C_3)} \right]$$

where: V_m = volume (meter)

P_b = atmospheric pressure

P_m = pressure at meter

Individual Probable Errors(8)

V_m; ± .004%

P_b; ± .21%

P_m; ± .42%

T_m; ± .10%

Then using Eq. 1,

E_s for $V_{m_{std}} = \pm 1.10\%$

In the same manner, the maximum probable error for scfm was found to be ± 3.2%. Laboratory analysis determined the weight measurements to be accurate ± 0.003% of the total weight. Table 6-7 shows the estimated error for each type of analysis. The effect of this error on the Total Air Emission figure was negligible.

With maximum probable errors for mg, $V_{m_{std}}$, and scfm all known, Eqn. (1) is then evaluated using the procedure previously mentioned to yield a maximum probable error for the Total Air Emission figures.

Maximum Probable Error for Total Air Emission is ± 3.4%

TABLE 6-7

PROBABLE ANALYTICAL ERRORS

Parameter	Estimated Error	Source
Particulate analysis of organic emission tests		
probe wash	± 0.05 mg	EPA Method 5
cyclone	± 0.05 mg	EPA Method 5
filter	± 0.05 mg	EPA Method 5
condenser	± 0.05 mg	EPA Method 5
Benzene soluble residue tests (each train component)		
benzene solubles	± 0.05 mg	Estimate
particulate weight	± 0.05 mg	Estimate
Total Organic Carbon (in quench water)	± 2% mg/l)	Function of instrument
Total Hydrocarbons Benzene	± 1 ppm	Function of instrument
Biological Test	NA*	

* NA = Not Available

7.0 ANALYTICAL METHODS

7.1 Organic Emission Tests and Water Samples

Samples from the fifteen organic emission tests (plus one blank) were analyzed for particulate and organic content. Four water samples were also analyzed for organics.

Three tests (Nos. 5, 7, and 14) representing three different test conditions (clean water - green coke, clean water - nongreen coke, and contaminated water - nongreen coke) were analyzed by sampling train component. The analytical scheme for these tests is depicted in Figure 7-1. Particulate content was determined separately for each of three samples per test: The cyclone wash, probe wash, and filter. Then, soxhlet extractions were performed on the dried cyclone catch, dried probe wash plus filter, and the XAD-2 resin. The XAD-2 extract and methylene chloride extract of the condensate were combined. Three extracts (cyclone wash, probe wash plus filter, and XAD-2 resin plus condensate) were subsequently analyzed for organic content.

The other twelve tests and the blank were each analyzed similarly by train component for particulate. A composite sample of extracts from particulates, condensate, and XAD-2 resin was then used for organic analysis. These procedures are outlined in Figure 7-2.

EPA Level 1 analytical methods were followed for all of the described analyses.(9,10) The only exceptions are the Gas Chromatography/Mass Spectrometry analyses (GC/MS.(11,12)

7.1.1 Particulate

Total particulate was determined by drying each sample in a tared evaporating dish at 50°C and desiccating at room temperature to constant weight. These procedures were carried out under conditions of dim light and samples were subsequently stored in the dark at 4°C.

FIGURE 7-1

ANALYTICAL PROCEDURES FOR SAMPLES FROM TESTS 5, 7, AND 14

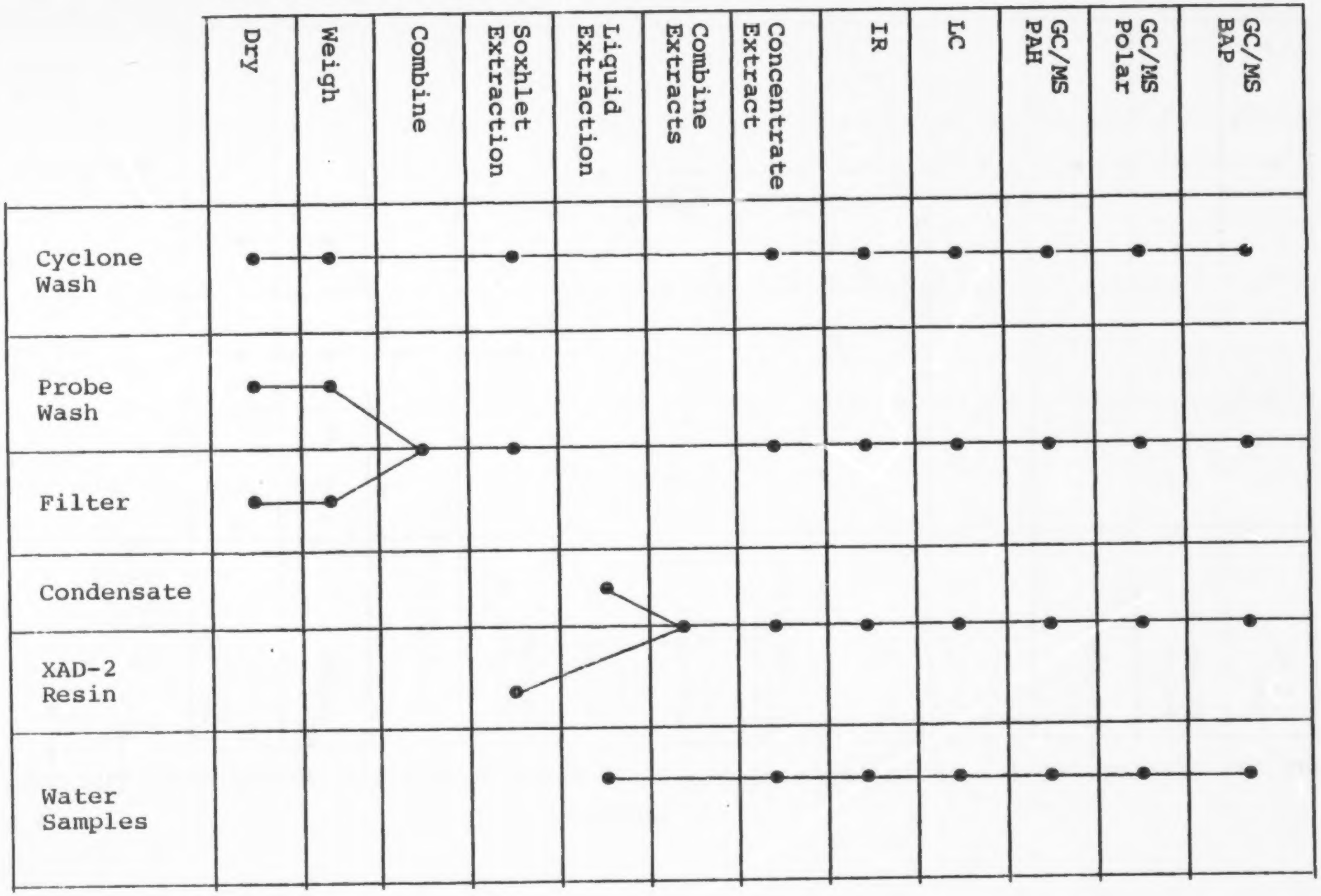
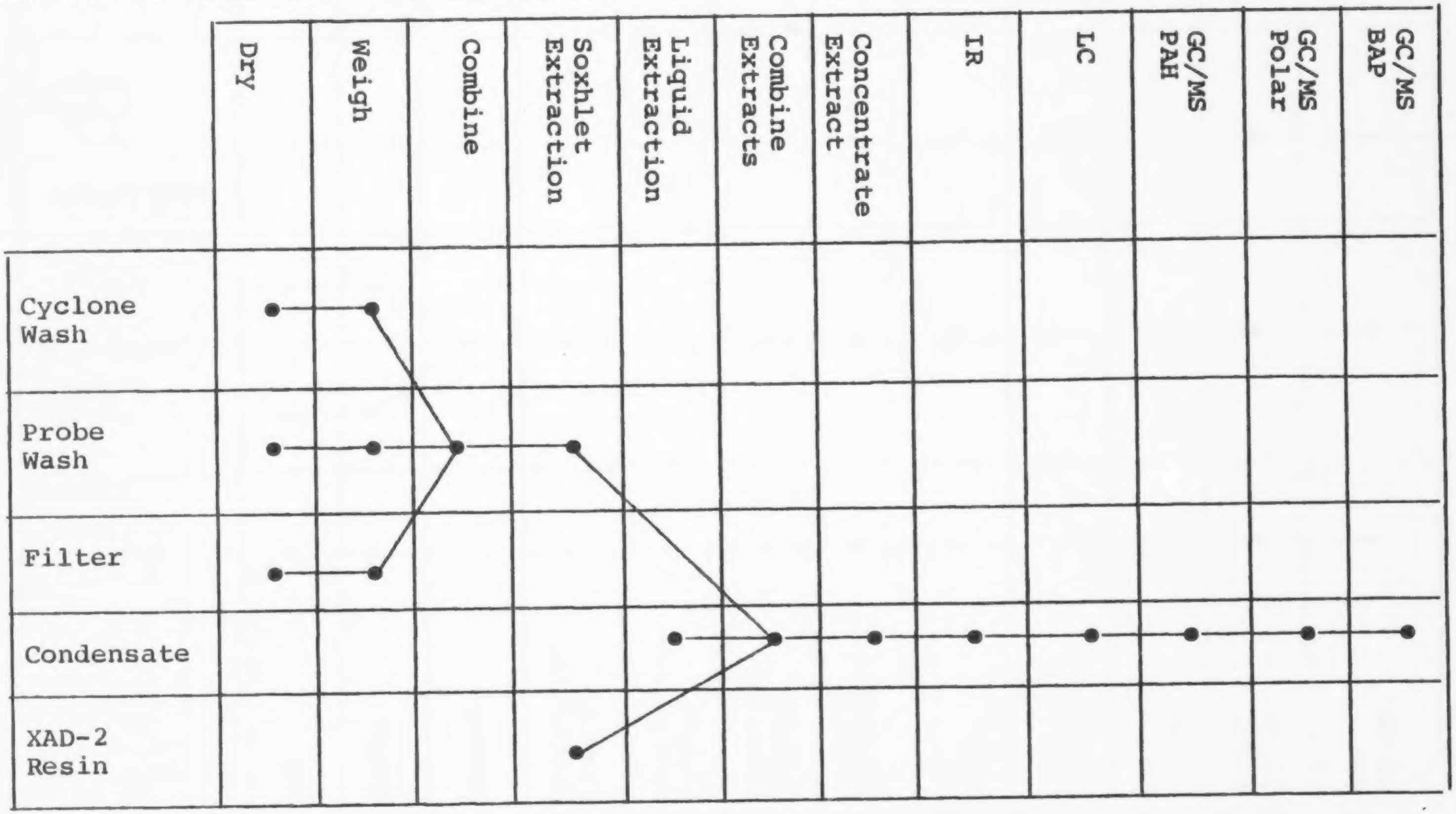

Dry
Weigh
Combine
Soxhlet Extraction
Liquid Extraction
Combine Extracts
Concentrate Extract
IR
LC
GC/MS PAH
GC/MS Polar
GC/MS BAP
Cyclone Wash
Probe Wash
Filter
Condensate
XAD-2 Resin
Water Samples

FIGURE 7-2

ANALYTICAL PROCEDURES FOR SAMPLES FROM TESTS 2B, 3, 4, 6, 8, 9, 10, 11, 12, 15, 16, AND 17


Dry
Weigh
Combine
Soxhlet Extraction
Liquid Extraction
Combine Extracts
Concentrate Extract
IR
LC
GC/MS PAH
GC/MS Polar
GC/MS BAP
Cyclone Wash
Probe Wash
Filter
Condensate
XAD-2 Resin

7.1.2 Sample Extraction

Samples were prepared for organic analysis by extraction with high purity methylene chloride (Burdick and Jackson, distilled-in-glass). Extraction was performed over a 24-hour period with about 500 ml of methylene chloride for XAD-2 resin samples and with about 300 ml methylene chloride for particulate samples. Four quench water samples (clean make-up and inlet, and contaminated make-up and inlet) were extracted with methylene chloride in separatory funnels fitted with Teflon stopcocks. The pH of the aqueous sample was adjusted to 2.8 with hydrochloric acid and then to 12.0 with sodium hydroxide. Two extractions were performed at each pH using a sample to methylene chloride ratio of about 20/1. The quench water extracts were then subjected to the same analyses described below.

7.1.3 T.C.O., GRAV, and IR

A Total Chromatographable Organics (T.C.O.) analysis was performed to determine the amount of organic material with boiling points from 100°C to 300°C in each sample. A gas chromatograph with flame ionization detector was used at the conditions shown in Table 7-1. The concentration of T.C.O. was calculated from the ratios of the peak areas of each sample to those of the known standards.

TABLE 7-1
INSTRUMENT CONDITIONS FOR T.C.O. ANALYSIS

Column:	10% OV-101 on 100/120 mesh Supelcoport
Injector temperature:	270°C
Detector temperature:	305°C
Temperature program:	Room temperature for 5 minutes, then programmed at 20°C/min up to 250°C
Gas flow rates:	He at 30 ml/min H_2 at 30 ml/min Air at 300 ml/min

A gravimetric analysis was performed for organic material with boiling points higher than 300°C. A one or five ml aliquot of sample extract was dried at room temperature in a desiccator to constant weight.

The Infrared (IR) spectra of all samples as potassium bromide micro pellets were obtained on a Perkin Elmer 521 grating spectrometer.

7.1.4 Liquid Chromatography (LC)

Subsequent analyses required another preparation step, Liquid Chromatography (LC). Samples were concentrated to 10 ml using Kuderna Danish apparatus then concentrated to 1 ml under a nitrogen stream and subjected to three consecutive solvent exchanges with cyclopentane. The cyclopentane solutions were chromatographed on a silica gel column. Seven fractions were collected by elution with solvent mixtures of increasing polarity.

Two extracts per sample were prepared for analysis by combining LC fractions 2,3, and 4 (aromatic) and fractions 5,6, and 7 (polar). This was necessary due to the large amounts of silicone grease and phthalates present in most of the samples (as shown by their IR spectra). The origin of these substances (in particular, whether or not they are sample contaminants) is not known. (See Section 8.2 for a detailed discussion.) However, their large quantity in most samples necessitated a reevaluation of future analytical procedures. An IR analysis of the EPA Level 1 LC fractions of two samples indicated that most of the silicone grease was found in fractions 2, 3, and 4 and that the phthalates were collected in fractions 5, 6, and 7. This separation of the silicone grease and phthalates allowed the IR spectra of other materials in the samples to be observed.

Therefore, all samples were separated into aromatic and polar fractions prior to further analysis.

Although the separation of silicone grease and phthalates aids in avoiding some analytical problems silicone grease may affect the LC procedure itself. During the concentration step prior to LC separation, the presence of silicone grease often prevented reduction of the extract to or below 10 ml. This will in effect raise the limit of detection for the GC/MS analyses. In addition, the large amounts of silicone grease present may alter the LC separation efficiency. If the LC separation becomes ineffective, the compounds for analysis may be spread throughout the LC fractions collected lowering the analytical levels observed for such samples in the combined extracts.

7.1.5 Low Resolution Mass Spectroscopy (LRMS)

LRMS was conducted on a Dupont 21-110B spectrometer. Samples were usually run at 15 ev and 70 ev ionization potentials over a temperature range of 70 - 350°C.

7.1.6 Gas Chromatography/Mass Spectrometry (GC/MS)

The two extracts obtained for each sample were subject to Gas Chromatography/Mass Spectrometry (GC/MS) analysis. For this, a Finnigan Model 4000 GC/MS system with a Finnigan Model 6110 data system was used. Each sample was separated into its component parts by GC, then specific organic compounds were identified and their concentrations determined by mass spectrometry.

The aromatic fractions were analyzed for a standard group of polycyclic aromatic hydrocarbons (PAH), ranging from fluorene to higher molecular weight aromatics. Analysis was also performed for other PAH compounds including lower molecular weight aromatics which were found in test 15 (a highly loaded sample). GC/MS conditions for these analyses are listed in Table 7-2. PAH species were identified by a calibration mixture which contained standards for most of the species analyzed. For those species not present in the calibration mixture, response factors were approximated from a linear regression analysis of the response factors of the materials in the calibration mixture as a function of molecular weight. This procedure is possible since it has been shown that the mass spectral response/weight for PAH's of quite different molecular weight has a nearly linear correlation with molecular weight. The lower molecular weight materials are subject to the highest analytical error and their values are likely to represent an over-estimation of their levels in the samples. Therefore, the levels of compounds with molecular weights below that of fluorene represent worst case levels.

The silicone grease present in most of the aromatic fractions would not be expected to interfere with the PAH analyses. Interferences in the GC/MS analysis are caused by coeluting compounds which have ions in common with the analytical ions of interest. Silicones tend to have few ions in common with PAH species.

The polar fractions were analyzed for heterocyclic oxygen and nitrogen compounds under the GC/MS conditions specified in Table 7-2. A highly loaded sample (Test 15) was again used as an indicator for compounds expected to be found in this fraction. Not all of the compounds detected in the survey sample were available for calibration standards. Six of the eighteen compounds identified were available in pure form (pyridine, aniline, phenol, cresol, quinoline, and acridine). Quantitation of nine more compounds (which are alkyl substituted derivatives of these six) was achieved

TABLE 7-2

OPERATING CONDITIONS FOR GC/MS ANALYSES

	PAH	Polar	BAP
GC CONDITIONS Column	Dexsil 400	Superpak 20M	SP-301 (liquid crystal)
Temperature program	Isothermal operation at 170° C for 1 min. Linear operation to 300°C at 15°C/min, isothermal operation at 300°C for 30 min.	Isothermal operation at 80°C for 1 min. Linear operation to to 250°C at 15°C/min, thermal operation at 250°C for 30 min.	Isothermal operation at 260°C.
Helium flow rate	30 mL/min	30 mL/min	30 mL/min
Sample Size	2 - 4 μL	1 - 2 μL	2 μL
Internal Std	9-phenyl anthracene	9-phenyl anthracene	9-10-diphenyl anthracene
MS CONDITIONS Mass Ranges	70-210, 211-270, 271-350	70-210, 211-270, 271-350	240-260 320-340
Integration Times	2, 5, 13	2, 5, 13	25, 25
Electron Multiplier Voltage	1800 V	1400 V	1500 V
Electron Energy	50 V	50V	50 V
Filament Emission	45 ma	45 ma	45 ma
Scan Rate	1 sec/spectrum	1 sec/spectrum	1 sec/spectrum

through using the unsubstituted compound as a model. The similarity in the mass spectra of the model and the substituted analog, and the generally flat system response within this range allow this method of quantitation. Calibration values were approximated for the few other compounds (i.e., benzonitrile, toluidine, and indole) by again finding models in the calibration mixture with similar mass spectra and spectral sensitivities. These calibration procedures lead to a higher relative error in the reported absolute values, a factor of 2 or 3 for the substituted analogs and a factor of 5 for the other few compounds. Their relative values remain quite accurate, however.

A separate GC/MS analysis, specific for benzo (a) pyrene, was also performed on each aromatic fraction. The operating conditions listed in Table 7-2 allow benzo (a) pyrene to be selectively separated from the other PAH species. The sensitivity and accuracy of the GC/MS system are improved with this analysis.

7.2 Benzene Soluble Residue Tests

All samples from the three benzene soluble residue tests were analyzed for both benzene soluble residue and particulate.

The cyclone catch, probe wash, and condenser catch from each test were analyzed in the same manner. Each sample contained water and benzene fractions. The entire sample was extracted with benzene. The water layer was evaporated to dryness at 103°C, desiccated and weighed to constant weight for a particulate determination. Insoluble particulate was filtered from the benzene layer and the benzene fraction was then evaporated at room temperature, desiccated and taken to constant weight for determination of benzene soluble residue. The particulate weight of each sample was found by adding the particulate weight from the water fraction, plus benzene-in-soluble particulate and benzene soluble residue from the benzene fraction.

The filter and adsorber from each train were Soxhlet extracted with benzene according to Parma Standard Test Methods, Union Carbide Corporation (PSM-1013). Particulate weight for the filter was found by adding the benzene-insoluble particulate to the benzene soluble residue. The benzene soluble weight for the adsorber was also called "particulate" and added into the total particulate weight for each train.

7.3 Benzene and Total Hydrocarbons

Two grab samples of coke quench tower emissions were analyzed using a gas chromatograph with flame ionization detector for determination of Total Hydrocarbons (T.H.C.) and benzene.

7.4 Total Organic Carbon in Quench Water

Total Organic Carbon (T.O.C.) in clean and contaminated quench water (makeup to the sump and inlet) was automatically determined by a Dohrmann Envirotech Total Organic Carbon Analyzer. The results were read directly as mg/liter T.O.C.

7.5 Electrical Conductivity of Quench Water

These tests were conducted on the sump at the Lorain Plant. A Hach Meter was used and measurements were taken in micromhos/cm.

7.6 Biological Test

A composite sample was prepared by extraction with methylene chloride of the filter; the distilled water wash of the probe, cyclone, condenser, and the porous polymer (XAD-2) adsorbent trap. The extraction procedures followed the protocol outlined in the "Technical Manual for Analysis of Organic Materials in Process Streams" (13), and were approved by EPA.

The combined sample was prepared for the Ames bacterial assay and the clonal cytotoxicity assay by solvent exchange with dimethyl sulfoxide (DMSO) and concentration to 3 ml. These analyses were performed by Litton Bionetics, Inc.(14)

7.6.1 Ames Bacterial Assay

Mutagenicity potential of the sample was determined by a test of its genetic activity as indicated by its ability to revert certain Salmonella strains from histidine dependence to histidine independence, with and without mammalian metabolic activation. The number of revertants observed on the histidine-free medium reflects the degree of genetic activity.

The test conditions for the Ames Mutagenicity Assay are described in Table 7-3.

Approximately 10^8 cells from an overnight culture of each indicator strain were added to separate test tubes containing 2.0 ml molten agar supplemented with biotin and a trace of histidine. For nonactivation tests, 0.01, 0.1, 1.0 and 10 ml/plate were added to the contents of the appropriate tubes and poured over the surfaces of selective agar plates. In activation tests, four dose levels of the test chemical were added to the appropriate tubes with cells. Just prior to pouring, an aliquot of reaction mixture (0.5 ml containing the 9,000 x g liver homogenate) was added to each of the activation overlay tubes which were then mixed, and the contents poured over the surface of a minimal agar plate and allowed to solidify. The plates were incubated for 48 hr at 37°C and scored for the number of colonies growing on each plate. Positive and solvent controls using both directly positive chemicals and those that require metabolic activation were run with each assay.

A toxicity test was performed at each dose level with and without metabolic activation. The methodology is similar to the plate test method described above, except that approximately 200 cells instead of 10^8 were used. The Vogel-Bonner

TABLE 7-3

AMES MUTAGENICITY ASSAY
TEST CONDITIONS

1) Indicator Micro-organisms: Salmonella Typhimurium

Salmonella strains :
TA-1535
TA-1537
TA-98
TA-100

2) Activation System:

a) Reaction mixture

Component	Final Concentration/ml
TPN (sodium salt)	4 µl/moles
Glucose -6-phosphate	5 µl/moles
Sodium phosphate (dibasic)	100 µl/moles
$MgCl_2$	8 µl/moles
KCl	33 µl/moles

b) S9 homogenate

A 9,000 x g supernatant was prepared from Sprague-Dawley adult male rate liver induced by Aroclor 1254 five days prior to kill according to the procedure of Ames *et al*. (1975). S9 samples were coded by lot number and assayed mg protein/ml and relative P448/P450 activity by methods described in LBI Technical Data on Rat Liver S9 Product.

3) Positive Control Chemicals

Salmonella strain	Chemical	Dose
TA-1535 TA-100	N-Methyl,N-Nitro,N-Nitrosoguandidine	1 µg/plate
TA-1537	9-Aminoacridine	50 µg/plate
TA-98	2-Nitro fluorene	10 µg/plate

minimal glucose agar plates were replaced by the standard method nutrient agar plates.

The numbers of colonies on each plate were counted and recorded. These raw data were analyzed in a computer program for revertants/plate (mutagenicity assays) and population/plate (toxicity assays) for each indicator strain.

7.6.2 Clonal Cytotoxicity Assay

The cytotoxicity of the coke quench tower emission sample was determined by measuring the reduction in colony-forming ability of cultured chinese hamster cells (CHO). Following 24 hours exposure to the sample and a period of recovery and growth, the number of colonies present in treated cultures was compared to the number in untreated cultures. The concentration of test material responsible for a 50% reduction in colony number was estimated and referred to as the EC50 value.

A chinese hamster cell line, CHO-KI (ATCC No. CCL 61), was used for this assay. The cell type was originally derived from ovarian tissue and has spontaneously transformed to a hypo-diploid line of rounded, fibroblastic cells with unlimited growth potential. Monolayer cultures have a fast doubling time of 10 to 12 hours and untreated cells can normally be cloned with an efficiency of 80% or greater. The CHO-KI cell line was maintained in Ham's F12 culture medium, containing 3×10^{-4} M L-proline (the cell line has an absolute requirement for proline), and supplemented with 10% fetal bovine serum, 100 units/ml penicillin, and 100 μg/ml streptomycin.

Cells from a monolayer stock culture were trypsinized, counted by hemocytometer, and reseeded into a series of

100 mm culture dishes at 500 cells/dish. Each dish contained 10 ml of growth medium. The cultures were incubated overnight at 37°C to allow attachment of the cells and recovery of growth rate.

A volume of 2.2 ml of test material was combined with 7.8 ml of growth medium to yield a stock concentration of 220 µl/ml. Other stocks were prepared by dilutions with growth medium such that 1 ml additions to the 10 ml cell cultures would yield the following final concentrations: 20 µl/ml,10 µl/ml, 5 µl/ml, 2 µl/ml and 0.5 µl/ml.

Each concentration of test material was applied to three culture dishes. After a 24-hr exposure period the medium was aspirated and the cells washed twice with Hank's balanced solution (prewarmed to 37°C). Fresh medium (20 ml) was placed on each culture, and incubation continued for an additional 6 days to allow colony development.

Medium was drained from the cultures after the incubation period and the surviving colonies were washed with phosphate-buffered saline (PBS), fixed in methanol, and stained with Giemsa. Colonies were counted by eye; tiny colonies of approximately 50 to 100 cells were excluded.

The controls consisted of one culture of untreated cells and two cultures exposed to DMSO (solvent control) at a final concentration of 20 µl/ml (20% by volume). DMSO in the treated cultures was a maximum of 2% at the highest concentration of test material. The solvent control dishes provided the reference cloning efficiency for determining the effect of the test material.

8.0 ORGANIC EMISSIONS

8.1 Organic Emission Test Results

The results of the organic emission tests are presented in Tables 8-2 to 8-8. Values for individual organic species are given in $\mu g/m^3$ and grams/metric ton of coal as determined by GC/MS analysis. Results of the TCO, gravimetric, infrared and LRMS analyses are not available due to interference from the large amounts of silicone and phthalates in the samples. Total organic emissions from the quench tower are therefore unknown since all of the organics could not be quantified.

Polycyclic aromatic hydrocarbons were found in the emission samples in substantial quantities as shown in Tables 8-2 and 8-3. Compounds which together contributed an average of 80% (at least 64%) of the total PAH for each clean water test are:

1) Naphthalene
2) Methyl Naphthalenes
3) Acenaphthylene/Biphenylene
4) Dimethyl Naphthalenes
5) Fluorene
6) Dibenzofuran/Methyl Biphenyl
7) Anthracene/Phenanthrene
8) Methyl Anthracenes

The major contributors in contaminated water tests include all of the above except dimethyl naphthalenes and methyl anthracenes. These major compounds account for an average of 85% (at least 78%) of the total PAH in contaminated water tests. The primary contributor among these is naphthalene. These organic species are of lower molecular weight, ranging from m/e 128 to m/e 192.

Polar compound results are reported in Tables 8-4 and 8-5 and also show substantial concentrations to be present. In particular, phenol is the primary constituent in the clean water tests and phenol, cresol, methyl cresol, and quinoline are major contributors in the contaminated water tests.

The average concentrations of PAH and polar compunds in coke quench tower emissions are shown according to process condition in Table 8-1.

TABLE 8-1

ORGANIC EMISSIONS SUMMARY

	Clean Water		Contaminated Water	
	$\mu g/m^3$	grams/metric ton of coal	$\mu g/m^3$	grams/metric ton of coal
Total PAH:				
average	767	0.758	31,000	32.1
(range)	(170-1900)	(0.156-1.90)	(13,700-47,300)	(15.5-46.4)
Green coke	1160	1.17		
	(660-1900)	(0.679-1.90)	-	-
Nongreen coke	442	0.419	31,000	32.1
	(170-745)	(0.156-0.646)	(13,700-47,300)	(15.5-46.4)
Polar Fraction:				
average	771	1.10	540,000	581
(range)	(60-6090)	(0.0575-6.89)	(243,000-922,000)	(185-1009)
Green coke	1540	1.70		
	(118-6090)	(0.119-6.89)	-	-
Nongreen coke	134	0.606	540,000	581
	(60-253)	(0.0575-3.13)	(243,000-922,000)	(185-1009)

An increase in organic emissions is distinctly shown for both PAH (∿ 40 times) and polar materials (∿ 500 times) when contaminated water is in use. This trend also appears with the use of green coke where a threefold increase is found for both PAH and polar compounds.

The test results for the three sampling trains analyzed by component are summarized in Tables 8-6 and 8-7. Most of the PAH material found for each test was in the organic adsorber unit, meaning that this material is smaller than 0.3 micrometers (or it would have been caught on the filter). Tests by Broddin et al have shown that "over 90% of polycyclic aromatic hydrocarbons is found on the particles smaller than 3 μm which means that most of these compounds are within the respiratory size range.(15) It should be noted that organic species of higher molecular weight (m/e > 216) were found in the cyclone samples (which contain larger size particles) but not in the filter samples. Most PAH compounds that have been determined to be carcinogenic do have a molecular weight greater than 216.

The GC/MS analysis specific for benzo(a) pyrene (BaP) generated the results found on Table 8-8. BaP in quench tower emissions is four times greater when contaminated water is in use (0.081 g/metric ton of coal) than clean water (0.019 g/metric ton of coal). However, the BaP data are very scattered in regards to coke greenness.

A number of the organic compounds detected in the coke quench tower emission tests exceeded the Minimum Acute Toxicity Effluent (MATE) values for health for some tests(16). These compounds also showed a high "Degree of Hazard"(17). The compounds are identified in Table 8-9 along with the process

TABLE 8-2

POLYCYCLIC AROMATIC HYDROCARBONS

μg/m^3

m/e	Species	CLEAN WATER TESTS											CONTAMINATED WATER TESTS			
	Test #	7	10	9	4	6	8	2B	11	3	12	5	16	15	17	14
	Greeness	1.2	1.5	1.6	1.6	1.6	1.8	3.4	3.2	3.3	3.7	4.0	0.3	0.5	0.5	1.5
116	Indene												273	31.3	165	69
128	Naphthalene	99	81.7	80.8	103	74.5	212	135	109	249	527	173	24100	26330	8510	> 6846
134	Benzothiophene	2.3					1.39					4.2	980	1030	311	937
142	Methyl Naphthalenes	25	9.86	20.2	18.2	17.6	62.1	78.8	25.6	52.1	216	82	1850	1540	424	1631
152	Acenaphthylene/Biphenylene	11	1.34		6.41	10.1	16.5	28.8	10.3	71.5	90.3	31	3750	3850	1110	1892
154	Biphenyl	6.8					5.19	8.75		25.5	20.4	10.9	304	333	68.6	345
156	Dimethyl Naphthalenes	25	4.75	27.6			54.3	114	189	34.5	233	135	315	269	68.1	352
166	Fluorene	35		18.1		3.97	51.6	38.6	11.5	41.8	71.7	70	2800	3540	778	2190
167	Carbazole												276	550	229	470
168	Dibenzofuran/methyl biphenyl	18		23.2		4.57	5.52	57.4		70.1		69	1100	1260	262	1274
178	Anthracene/phenanthrene	260	37.0	164	42.5	52.4	86.5	140	116	86.7	285	478	3070	4990	997	> 4005
184	Dibenzothiophene	16		11.6								10	139	280	39.3	219
192	Methyl anthracenes	85	27.1	109		49.6	16.4	83.2	143	67.2	208	183	237	419	75.2	410
202	Fluoranthene	31	4.45	49.5		8.47	17.9	25.6	15.5	118	72.5	44	541	1150	247	918
202	Pyrene	29		33.1			28.7	19.8	27.4	143	72.5	38	474	1210	276	737
204	$C_{16}H_{12}$ PAH			8.39									10.3	15.8	3.32	46
204	$C_{16}H_{12}$ PAH												22.6	40.5	8.04	12
204	$C_{16}H_{12}$ PAH												5.27	9.61	2.45	
208	$C_{16}H_{16}$ PAH												7.38	21.9	5.14	11
216	Methyl Fluoranthenes Methyl Pyrenes	13		19.1		8.43		11.4		40.7	82.7	20	58.6	145	33.5	120
218	Dihydrobenzofluorene		30.4			34.7		5.75	9.69	20.1	14.4		34	81.3	13.2	42
228	Chrysene/Benz(a)anthracenes	89					9.19	3.13		8.79		11.4	44.6	81.3	26.6	88
234	Naphthobenzothiophene												.280	2.59	4.47	2.3
242	Methyl-chrysenes												13.6	17.8	10.0	14
252	Benzofluoranthenes Benzo (e) pyrene Benzo (a) pyrene												52.3	88.9	28.4	118
252	Perylene											84				76
254	9-phenyl anthracene (IS)															
256	7,12 Dimethyl Benz (a) anthracene															
266	Methyl-benzo pyrenes															
267	Dibenzo (c,g) carbazole															
268	3-methyl cholanthrene		14.9	18.2		29.0			11.1	14.2	15		7.71	2.41	12.3	
276	Indeno (1,2,3-cd)pyrene			11.4									7.00		5.09	
276	Benzo (ghi) perylene		16.1	26.3		29.8								.783		
278	Dibenzo (a,h) anthracene															
300	Coronene															
302	Dibenzo (ai & ah) pyrenes															
	TOTAL	745	227	620	170	323	565	745	660	1040	1900	1443	40500	47300	13700	22844

Note: Polynuclear Aromatic Hydrocarbons were measured by Gas Chromatography/Mass Spectrometry. All blanks indicate that the concentration of the species was below the detection level. The detection limit for each PAH species varies with molecular weight, reaching differences from five to twenty times with a lower limit at naphthalene and a higher limit at coronene. This "upper limit" for each test is given below:

Detection Limit in μg/m^3	≤90	≤116	≤102	≤84	≤98	≤76	≤78	≤102	≤72	≤92	≤104	≤110	≤76	≤77	≤61

TABLE 8-3
POLYCYCLIC AROMATIC HYDROCARBONS
(grams/metric ton of coal)

		CLEAN WATER TESTS											CONTAMINATED WATER TESTS			
	Test #	7	10	9	4	6	8	2B	11	3	12	5	16	15	17	14
m/e	Species Greeness	1.2	1.5	1.6	1.6	1.6	1.8	3.4	3.2	3.3	3.7	4.0	0.3	0.5	0.5	1.5
116	Indene												0.263	0.0307	0.186	0.0830
128	Naphthalene	0.0895	0.0750	0.0770	0.0945	0.0815	0.181	0.135	0.112	0.282	0.525	0.159	23.2	25.8	9.60	8.30
134	Benzothiophene	0.00198					0.00119					0.00400	0.940	1.01	0.349	1.14
142	Methyl Naphthalenes	0.0219	0.0100	0.0192	0.0168	0.0193	0.0530	0.0785	0.0263	0.0590	0.216	0.0750	1.78	1.51	0.477	1.98
152	Acenaphthylene/Biphenylene	0.00970	0.00126		0.00590	0.0110	0.0141	0.0288	0.0106	0.0810	0.0895	0.0290	3.62	3.77	1.25	2.28
154	Biphenyl	0.00590					0.00500	0.00870		0.0288	0.0204	0.0100	0.293	0.326	0.0770	0.412
156	Dimethyl Naphthalenes	0.0211	0.00500	0.0263			0.0462	0.114	0.193	0.0393	0.232	0.124	0.303	0.264	0.0765	0.424
166	Fluorene	0.0308		0.0173		0.00432	0.0443	0.0385	0.0118	0.0474	0.0715	0.0635	2.69	3.47	0.875	2.65
167	Carbazole												0.266	0.539	0.258	0.565
168	Dibenzofuran/methyl biphenyl	0.0158		0.0222		0.00496	0.00500	0.0575		0.0795		0.0625	1.06	1.23	0.294	1.54
178	Anthracene/phenanthrene	0.224	0.0350	0.156	0.0390	0.0570	0.0735	0.140	0.113	0.0975	0.283	0.435	2.95	4.91	1.12	4.85
184	Dibenzothiophene	0.0135		0.0111								0.00950	0.134	0.274	0.0443	0.246
192	Methyl anthracenes	0.0730	0.0250	0.104		0.0540	0.0140	0.0830	0.147	0.0760	0.206	0.169	0.228	0.412	0.0845	0.496
202	Fluoranthene	0.0268	0.00500	0.0470		0.0925	0.0155	0.0256	0.0159	0.134	0.0720	0.0400	0.520	1.13	0.278	1.14
202	Pyrene	0.0246		0.0303			0.0245	0.0198	0.028	0.162	0.0720	0.0345	0.454	1.18	0.309	0.890
204	$C_{16}H_{12}$ PAH			0.00790									0.00990	0.0155	0.00382	0.0555
204	$C_{16}H_{12}$ PAH												0.0217	0.0396	0.00915	0.0141
204	$C_{16}H_{12}$ PAH												0.00505	0.00940	0.00267	
208	$C_{16}H_{16}$ PAH												0.00710	0.0215	0.00575	0.0134
216	Methyl Fluoranthenes Methyl Pyrenes	0.0112		0.0182		0.00920		0.0114		0.0462	0.0820	0.0185	0.0565	0.143	0.0374	0.145
218	Dihydrobenzofluorene		0.0300			0.0379		0.00575	0.00993	0.0227	0.0144		0.0327	0.0795	0.0149	0.0496
228	Chrysene/Benz (a) anthracenes	0.0765					0.00800	0.00312		0.00995		0.0105	0.0430	0.0795	0.0302	0.107
234	Naphthobenzothiophene												0.000269	0.00254	0.00496	0.0027
242	Methyl-chrysenes												0.0130	0.0174	0.0115	0.0167
252	Benzofluoranthenes Benzo (e) pyrene Benzo (a) pyrene												0.0500	0.0870	0.0321	0.143
252	Perylene											0.0770				0.0910
254	9-phenyl anthracene (IS)															
256	7,12 Dimethyl Benz (a) anthracene															
266	Methyl-benzo pyrenes															
267	Dibenzo (c,g) carbazole															
268	3-methyl cholanthrene		0.0150	0.0174		0.0317			0.0114	0.0161	0.0149		0.00740	0.00236	0.0138	
276	Indeno (1,2,3-cd) pyrene			0.0109									0.00670	0.000770	0.00575	
276	Benzo (ghi) perylene		0.0150	0.0251		0.0326										
278	Dibenzo (a,h) anthracene															
300	Coronene															
302	Dibenzo (ai & ah) pyrenes															
	TOTAL	0.646	0.216	0.590	0.156	0.436	0.485	0.750	0.679	1.18	1.90	1.32	39.0	46.4	15.5	27.6

NOTE: Polynuclear Aromatic Hydrocarbons were measured by Gas Chromatography/Mass Spectrometry. All blanks indicate that the concentration of the species was below the detection level.

TABLE 8-4

POLAR FRACTION

($\mu g/m^3$)

	CLEAN WATER											CONTAMINATED WATER			
	Test #	7	10	9	4	6	8	2B	11	3	12	5	16	15	17	14
m/e Species	Greeness	1.2	1.5	1.6	1.6	1.6	1.8	1.8	3.2	3.3	3.7	4.0	0.3	0.5	0.5	1.5
79 Pyridine		37.6										2.76	4810	14700	2610	25900
93 Methyl Pyridine		1.66										4.32	2120	5300	2510	22700
93 Aniline		0.952										0.560	1610	3510	679	4640
94 Phenol		77.3	181	60.1	179	90.4	75.2	118	779	2830	78.4	0.143	88800	503000	59600	272000
103 Benzonitrile													2730	1800	1490	3970
107 Dimethyl/ethyl pyridine		1.65											750	12400	1520	14200
107 Toluidine		0.47											975	554	176	2060
108 Cresol							23.6		30.0	2800	98.6		103000	349000	75100	404000
117 Indole													341	641	1330	3200
121 Trimethyl pyridine												128	885	2950	376	2230
122 Methyl cresol										329			13400		11800	34800
129 Quinoline									61.1	132	19.5	0.118	9430	25500	6430	36300
129 Isoquinoline												0.118	8030	967		490
136 Trimethyl phenol																1570
143 Methyl quinoline			72.1						272				920	1570	614	3800
149 Phthalates*		>15500	> 2860	>1570	>4470	>3970	>1640	>18400	> 13800	>16200	>5380	>9.490	>109000	> 152000	>111000	>72800
157 Dimethyl/ethyl quinoline														232		390
179 Acridine																2.41
254 9-Phenylanthracene (IS)																

* Phthalates are considered to be a contaminant.

Note: All blanks indicate that the concentration of the species was below the detection level. The detection limit for each PAH species varies with molecular weight, reaching differences from five to twenty times with a lower limit at naphthalene and a higher limit at coronene. This "upper limit" for each test is given below:

Detection Limit in $\mu g/m^3$	≤90	≤116	≤102	≤84	≤98	≤76	≤78	≤102	≤72	≤92	≤104	≤110	≤76	≤77	≤61

TABLE 8-5
POLAR FRACTION
(grams/metric ton of coal)

m/e	Species	CLEAN WATER											CONTAMINATED WATER			
	Test #	7	10	9	4	6	8	2B	11	3	12	5	16	15	17	14
	Greeness	1.2	1.5	1.6	1.6	1.6	1.8	3.4	3.2	3.3	3.7	4.0	0.3	0.5	0.5	1.5
79	Pyridine	0.0324										0.00253	4.61	14.4	2.94	31.2
93	Methyl Pyridine	0.00143										0.00397	2.04	5.20	2.83	27.5
93	Aniline	0.000805										0.000489	1.54	3.44	0.765	5.60
94	Phenol	0.0670	2.24	0.0575	0.165	0.0990	0.0640	0.119	0.799	3.20	0.0780	0.000123	85.0	491	67.0	330
103	Benzonitrile												2.62	1.76	1.67	4.79
107	Dimethyl/ethyl pyridine	0.00141											0.720	12.2	1.70	17.1
107	Toluidine	0.000393											0.935	0.540	0.200	2.49
108	Cresol						0.0202		0.0308	3.17	0.0975		98.5	342	84.5	490
117	Indole												0.328	0.630	1.50	3.87
121	Trimethyl pyridine											0.117	0.850	2.89	0.425	2.70
122	Methyl cresol									0.372			12.9		13.3	42.1
129	Quinoline								0.0625	0.150	0.0194	0.0000980	9.045	25.0	7.25	43.8
129	Isoquinoline											0.0000980	7.70	0.945		0.590
136	Trimethyl phenol															1.90
143	Methyl quinoline		0.890						0.278				0.885	1.54	0.690	4.59
149	Phthalates*	>13.3	>3.53	>1.50	>4.12	>4.35	>1.40	>18.4	>14.1	>18.4	>5.35	>8.70	>105	>149	>125	>70.0
157	Dimethyl/ethyl quinoline													0.228		0.472
179	Acridine															0.00291
254	9-phenylanthracene (IS)															

All blanks indicate that the concentration of the species was below the detection level.

* Phthalates are considered to be a contaminant.

TABLE 6-6

ORGANIC ANALYSIS OF TRAIN COMPONENTS

($\mu g/m^3$)

Species	Test No. 5 clean water coke greeness = 4.0			Test No. 7 clean water coke greeness = 1.2			Test No. 14 contaminated water coke greeness = 1.5		
	cyclone extract	filter and probe wash extract	XAD-2 extract	cyclone extract	filter and probe wash extract	XAD-2 extract	cyclone extract	filter and probe wash extract	XAD-2 extract
Polynuclear Aromatic Hydrocarbons									
Indene									69
Naphthalene	3.4	3.6	166	2.4	6.1	91	2.5	2.9	6840
Benzothiophene		0.60	3.6			2.30			937
Methyl Naphthalenes			32			25	1.42		1630
Acenaphthylene/Biphenylene			31			11.3	2.3		1890
Biphenyl		0.96	10		2.7	4.1	1.11		344
Dimethyl Naphthalenes			135			25			352
Fluorene	2.4	15	53	2.4	5.8	27	40	39	2110
Carbazole							98		372
Dibenzofuran/methyl biphenyl		1.71	67			18	8.1	6.4	1260
Anthracene/phenanthrene	48	150	280	114		146	465	390	3150
Dibenzothiophene		3.0	7.3	2.7	13		28		191
Methyl anthracenes	7.9	1.44	174			85	36	24	350
Fluoranthene	18	10	16	13	10	8.3	85	33	821
Pyrene	22		16	6.1	9.6	13	95	14	628
$C_{16}H_{12}$ PAH									46
$C_{16}H_{12}$ PAH									12
$C_{16}H_{12}$ PAH									
$C_{16}H_{16}$ PAH									11
Methyl Fluoranthene & Methyl Pyrene	3.9		16	0.18		13	26		34
Dihydrobenzofluorene							8.5		33
Chrysene/Benz(a)Anthracenes	4.9	0.15	6.4	1.4	93	4.4	49		39
Naphthobenzothiophene									2.26
Methyl-chrysenes							10		3.6
Benzofluoranthene, benzo(e) pyrene									
Benzo(a) pyrene							67		51
Perylene			84				76		
9-phenyl anthracene (IS)									
7,12 Dimethyl Benz(a) anthracene									
Methyl-benzo pyrenes									
Dibenzo (c,g) carbazole									
3-methyl cholanthrene									
Indeno (1,2,3-cd) pyrene									
Benzo (ghi) perylene									
Dibenzo (a,h) anthracene									
Coronene									
Dibenzo (ai & ah) pyrenes									
Total	110	186	1147	142	130	473	26	509	21236
Polar Compounds									
Pyridine	1.51	0.244	1.01	11.7	0.66	25.2		65.1	25800
Methyl Pyridine	2.64		1.68		1.66				22700
Aniline	0.340	0.220			0.223	0.729	1.98		4640
Phenol		0.143		64.5		12.8		455	272000
Benzonitrile									3970
Dimethyl/ethyl pyridine					1.65				14200
Toluidine					0.47			0.363	2060
Cresol									404000
Indole								51.0	3150
Trimethyl pyridine	128								2230
Methyl cresol									34800
Quinoline			0.118						36300
Isoquinoline			0.118				14.1		475
Trimethyl phenol									1570
Methyl quinoline							9.49		3790
Phthalates*	>4080	>2530	>2880	>7800	>4900	>2750	>16900	>11200	>44700
Dimethyl/ethyl quinoline									390
Acridine								2.41	
9-phenylanthracene (IS)									
Benzo(a) pyrene**	26		38				55	19	24

* Phthalates are considered to be a contaminant.

** These results were obtained from a special analysis with high sensitivity for benzo(a)pyrene.

Note: All blanks indicate that the concentration of the species was below the detection level. The detection limit for each PAH species varies with molecular weight, reaching differences from five to twenty times with a lower limit a naphthalene and a higher limit at coronene. This "upper limit" for each component is given below:

Detection Limit in $\mu g/m^3$	≤74	≤64	≤104	≤78	≤68	≤90	≤52	≤52	≤61

TABLE 8-7

ORGANIC ANALYSIS OF TRAIN COMPONENTS
(grams/metric ton of coal)

Species	Test No. 5 clean water coke greeness=4.0			Test No. 7 clean water coke greeness=1.2			Test No. 14 contam. water coke greeness=1.5		
	cyclone extract	filter and probe wash extract	XAD-2 extract	cyclone extract	filter and probe wash extract	XAD-2 extract	cyclone extract	filter and probe wash extract	XAD-2 extract
Polynuclear Aromatic Hydrocarbons									
Indene									0.0830
Naphthalene	0.00300	0.00350	0.152	0.00200	0.00500	0.0780	0.00336	0.00356	8.30
Benzothiophene		0.000500	0.00350			0.00200			1.14
Methyl Naphthalenes			0.0750			0.0220	0.00172		1.98
Acenaphthylene/Biphenylene			0.0290			0.00950	0.00275		2.28
Biphenyl		0.00100	0.00900		0.00250	0.00350	0.00135		0.412
Dimethyl Naphthalenes			0.123			0.0210			0.424
Fluorene	0.00200	0.0135	0.0480	0.00200	0.00500	0.0235	0.0485	0.0470	2.56
Carbazole							0.118		0.447
Dibenzofuran/methyl biphenyl		0.00150	0.0610			0.0155	0.00975	0.00775	1.52
Anthracene/phenanthrene	0.0440	0.137	0.256	0.0985		0.125	0.560	0.470	3.81
Dibenzothiophene		0.00300	0.00650	0.00250	0.0110		0.0334		0.214
Methyl anthracenes	0.00700	0.00150	0.159			0.0730	0.0435	0.0290	0.424
Fluoranthene	0.0165	0.00950	0.0145	0.00100	0.00850	0.00700	0.103	0.0404	0.990
Pyrene	0.0200		0.0145	0.00500	0.00800	0.0110	0.115	0.0170	0.760
$C_{16}H_{12}$ PAH									0.0555
$C_{16}H_{12}$ PAH									0.0141
$C_{16}H_{12}$ PAH									
$C_{16}H_{16}$ PAH									0.0134
Methyl Fluoranthene & Methyl Pyrene	0.00350		0.0150	0.000150		0.0110	0.0313		0.114
Dihydrobenzofluorene							0.0103		0.0395
Chrysene/Benz(a)Anthracenes	0.00450	0.00150	0.00600	0.00100	0.0715	0.00350	0.0590		0.0477
Naphthobenzothiophene									0.00274
Methyl-chrysenes							0.0123		0.00439
Benzofluoranthene, benzo(e)pyrene									
Benzo(a)pyrene							0.0810		0.062
Perylene			0.0770				0.0910		
p-phenyl anthracene (IS)									
7,12 Dimethyl Benz(a)anthracene									
Methyl-benzo pyrenes									
Dibenzo (c,g) carbazole									
Indeno (1,2,3-cd)pyrene									
Benzo (ghi) perylene									
Dibenzo (a,h) anthracene									
Coronene									
Dibenzo (ai & ah) pyrenes									
Total	0.101	0.173	1.05	0.112	0.112	0.406	1.33	0.615	25.7
Polar Compounds									
Pyridine	0.00138	0.000221	0.000910	0.0101	0.000555	0.0217		0.0610	31.2
Methyl Pyridine	0.00240		0.00155		0.00143				27.5
Aniline	0.000312	0.000196			0.000184	0.00062	0.00240		5.60
Phenol		0.000123		0.0555		0.0111		0.550	329
Benzonitrile									4.81
Dimethyl/ethyl pyridine					0.00141				17.1
Toluidine					0.000393			0.000439	2.49
Cresol									490
Indole								0.0615	3.80
Trimethyl pyridine	0.117								2.70
Methyl cresol									42.1
Quinoline			0.0000980						43.8
Isoquinoline			0.0000980				0.0170		0.575
Trimethyl phenol									1.90
Methyl quinoline							0.0115		4.58
Phthalates*	>3.72	>2.32	>2.64	>6.70	>4.20	>2.37	>2.055	>13.5	>54.0
Dimethyl/ethyl quinoline									0.474
Acridine								0.00291	
9-phenylanthracene (IS)									
Benzo(a)pyrene**	0.025		0.035				0.066	0.023	0.029

* Phthalates are considered to be a contaminant.

**These results were obtained from a special analysis with high sensitivity for benzo(a)pyrene.

TABLE 8-8

BENZO(A) PYRENE IN COKE QUENCH TOWER EMISSIONS

Test Number	Coke Greenness Rating	$\mu g/m^3$	g/metric Ton of Coal
CLEAN WATER TESTS			
7	1.2	*ND	
10	1.5	ND	
9	1.6	38	0.036
4	1.6	42	0.039
6	1.6	66	0.072
8	1.8	ND	
11	3.2	ND	
3	3.3	ND	
2B	3.4	ND	
12	3.7	ND	
5	4.0	66	0.060
CONTAMINATED WATER TESTS			
16	0.3	99	0.095
15	0.5	72	0.071
17	0.5	36	0.040
14	1.5	98	0.12

TESTS ANALYZED BY SAMPLING TRAIN COMPONENT

Component	Test 5		Test 7		Test 14	
	$\mu g/m^3$	g/metric ton of coal	$\mu g/m^3$	g/metric ton of coal	$\mu g/m^3$	g/metric ton of coal
Cyclone	28	0.025	ND	ND	55	0.066
Probe/Filter	ND		ND	ND	19	0.023
Adsorber	38	0.035	ND	ND	24	0.029
Total	66	0.060	ND	ND	98	0.12

* ND - Not Detected. The detection limits for the benzo(a)pyrene analysis for each test are as follows:

Test No.	2B	3	4	5	6	7	8	9	10	11	12	14	15	16	17
Detection Limit in $\mu g/m^3$: Total	8	7	8	10	10	9	8	10	12	10	9	6	8	11	8
Cyclone				7		8						5			
Probe/Filter				6		7						5			
Adsorber				10		9						6			

TABLE 8-9

ORGANIC SPECIES FOUND IN EMISSIONS AT LEVELS POTENTIALLY HARMFUL TO HEALTH

Species	Process Conditions Clean Water Nongreen Coke	Clean Water Green Coke	Contaminated Water Nongreen Coke
3-Methyl Cholanthrene	X	X	X
Benz (a) anthracene*	X		X
Phenanthrene			X
Benzo (a) pyrene			X
Phenol			X
Cresol			X
Quinoline			X

Note: X designates the presence of the species in emission tests under the noted process conditions.

*Assuming the total weight found at m/e 228 is attributable to benz(a) anthracene.

Species	Carcinogenic Potential	Hazard Potential
Benzo (a) pyrene	+++	XXX
3-Methyl cholanthrene	++++	XXX
7,12-Dimethyl benz (a) anthracene	++++	XXX
Dibenz (a,h) anthracene	+++	XXX
Dibenzo (a,h) pyrene	+++	
Dibenzo (a,i) pyrene	+++	XX
Benz (a) anthracene	+	XX
Pyridine		X
Indeno (1,2,3-cd) pyrene	+	

Rating system:
++, +++, or ++++ strongly carcinogenic
+ carcinogenic
XXX most hazardous
XX very hazardous
X hazardous

conditions under which they where found. It should be noted that other compounds were also present that fall into the categories labelled "carcinogens" by a Public Health Survey"(18) and "hazardous" by Multimedia Environmental Goals (MEGs)(16). These compounds are also identified in Table 8-9. Application of these four rating systems to the organic emission results has shown thirteen compounds present in quench tower emissions to be potentially harmful to some degree.

8.2 Sample Contamination

Silicone grease and phthalates were detected in coke quench tower samples by infrared analysis. The presence of these substances in each test is indicated in Tables 8-10 and 8-11. Although silicone grease and phthalates are considered sample contaminants for the purpose of this report, their origin and method of entry into the test samples is not well defined.

Silicone grease is reported in Table 8-10 as present in service water (#4), inlet water (#4), blank methylene chloride (trace) and blank water (trace) samples. It would have been difficult for the field test crew to contaminate the samples of water with silicone grease. It might be speculated that silicone grease could enter the water supply through its common use on pump and valve packing glands.

The presence of silicone grease in the cyclone catch of Test 5 (see Table 8-11) may also indicate some other source of contamination since silicone grease was used only on the condenser and impingers. No silicone grease was detected in the probe/filter samples for Tests 5, 7 and 14 which supports the statement that no silicone grease was used in the front half of the train.

TABLE 8-10

PRESENCE OF SILICONE GREASE AND PHTHALATES AS INDICATED BY IR

Test No.	Silicone Grease	Phthalates
2B	yes	yes
3	yes	yes
4	-	-
5	yes	-
6	yes	-
7	yes	yes
8	yes	-
9	yes	-
10	yes	-
11	yes	-
12	yes	-
14	yes	yes
15	yes	-
16	-	yes
17	yes	-
18	yes	yes
Service water (#4)	yes	-
Inlet water (#4)	yes	-
Liquor water (#9)	-	-
Inlet water (#9)	-	-
Blank methylene chloride	trace	
Blank water	trace	

TABLE 8-11

PRESENCE OF SILICONE GREASE AND PHTHALATES AS INDICATED BY IR

Sample	Silicone Grease	Phthalate
Test #5		
Cyclone	yes	-
Probe & Filter	-	-
XAD-2 Module	yes	-
Test #7		
Cyclone	-	yes
Probe & Filter	-	-
XAD-2 Module	yes	-
Test #14		
Cyclone	-	yes
Probe & Filter	-	yes
XAD-2 Module	yes	yes
Test #18	yes	yes

Phthalate was reported as a contaminant in three of the eleven clean water tests and in two of the four contaminated water tests (see Table 8-10). But phthalate was detected by GC/MS in some quantity in every one of the organic emission tests (from 1.4 to 149 grams per metric ton of coal). Phthalate was also found in the 1976 organic emission tests$^{(1)}$. At that time the most likely candidates were thought to be:

- Butyl benzyl phthalate
- Dimethyl cyclohexyl phthalate
- Mixed alcohol phthalates

Phthalatic acid would be one of the oxidation products of any benzene derivative having only two side-chains in the 0-position, such as the oxidation of naphthalene. Therefore some phthalates would be expected in coke quench tower emissions and phthalate has been measured in coke oven door leakage$^{(24)}$.

Although phthalate was present in all of the tests, in the contaminated water tests phthalates are present at levels of at least one order of magnitude greater than in the clean water tests (see Tables 8-4 and 8-5). This substantiates the theory that a significant portion of the phthalates may have come from coke oven processes.

8.3 Benzene Soluble Residue Test Results

The quantity of benzene soluble residue found in coke quench tower emissions appears to be substantial as shown in Table 8-12 with at least 234 grams per metric ton of coal. Most of the benzene solubles (at least 50%) were collected in the adsorber. Vaporous material and particles smaller than 0.3 micrometers are caught in this component.

TABLE 8-12

BENZENE SOLUBLE RESIDUE

Sample	mg/m^3	G/Metric Ton of Coal
Test No. 1 - clean,3[a]		
probe wash	38.2	42.3
cyclone	13.2	14.6
filter	3.95	4.35
condenser	1.26	1.39
adsorber	155	172
Total	212	234
Test No. 2 - clean,1.8		
probe wash	10.9	14.9
cyclone	5.19	7.10
filter[b]	no sample	
condenser[c]	101	138
adsorber	129	177
Total	246	337
Test No. 13 contaminated,1.5		
probe wash	18.0	17.6
cyclone	8.74	8.55
filter	38.7	38.0
condenser	81.6	80
adsorber	160	156
Total	307	300

[a] Quench water quality, Coke greenness

[b] Filter burned during test

[c] This benzene soluble sample appeared contaminated.

8.4 Benzene and Total Hydrocarbons (THC)

Benzene and THC concentrations detected in grab samples are given in Table 8-13.

TABLE 8-13

BENZENE AND THC EMISSIONS

	Date	ppm	grams/metric ton of coal
Benzene:	11/7/77	0.005	0.01
	11/8/77	0.040	0.13
THC:	11/7/77	8.54	30
(as Hexane)	11/8/77	17.34	60

Note: Clean quench water was in use on the test dates.

The concentrations of THC are comparable to the value of 12 ppm THC found in the 1976 Lorain tests(1).

8.5 Biological Test Results

One of the bioassays to which the coke quench tower biological sample was subjected is the Ames bacterial test for mutagenicity. Strains of Salmonella typhimurium unable to synthesize the amino acid histidine (due to a mutation, his$^-$) are used in the test. These bacteria cannot grow unless histidine is supplied to them. However, the event of a back mutation to his$^+$ would allow the bacteria to grow without the external histidine supply. The potential mutagenic properties of a material such as an extract of coke quench tower emissions may be tested in this way when the material is applied to his$^-$ bacteria. In addition, it is sometimes not the original form of such materials that is mutagenic, but one of its metabolites. Thus, the quench tower sample was also subjected to enzymes of a rat-liver extract (the site of major metabolic processes) in order that the sample metabolites also be tested.

The results of the Ames test are presented in Table 8-14. It is apparent that the number of revertant colonies is not significantly different from the solvent controls nor close to results for the positive controls. The test results for nonactivation and metabolic activation systems are negative(14).

Toxicity tests on the same strains of Salmonella were also performed and the results given in Table 8-14. The population counts may be compared to those of the solvent controls and positive controls to show that the test material was not toxic to any of the indicated organisms employed. It was noted in the original data that for nonactivation assay results for strain TA-1537 the solvent control colony counts were low, as were those for the highest dose of emission sample. This may be due to a technical error in diluting stock cells(14).

Another bioassay, the clonal cytotoxicity assay, was performed on the coke quench tower biological sample. This test measures the effects of varied doses of the sample on the colony forming ability of cultured Chinese hamster cells (CHO). The sample concentration that reduces the number of colonies by 50% (EC50 value] is determined and compared with defined toxicity levels.

The results of the clonal cytotoxicity assay are presented in Table 8-15. The original sample had been concentrated 8-fold prior to application to the test colonies, thus the "applied concentrations" are multiplied by 8 to obtain the original concentration values. The cloning efficiency of 72.0% for the untreated control culture indicates that the cells were in a healthy state and good cloning conditions were provided. The lower cloning efficiency of 59.4% for the solvent control may reflect artificially low colony numbers for this control since the number of colonies obtained with the lower concentrations of test material exceeded both the solvent and untreated controls(14).

Comparable numbers of colonies appear for the triplicate dishes at each sample concentration level, except for the original concentration of 4.0 µl/ml. The percent relative survival for each sample dose was derived from a comparison of the average number of colonies per test dish to the average number of colonies in the solvent control. These survival values were plotted in Figure 8-1 to estimate the sample's EC50 value. A smooth dose-response curve was obtained which passed through the 50% survival level at 100 µl/ml. However, the real position of the EC50 is likely to be less than 100 µl/ml since the survival curve itself rises far above the 100% survival level (reflecting the low colony count for the solvent control). Assuming that 153% survival at 4 µl/ml represents the true 100% survival level, the true EC50 would occur at 76% survival in Figure 8-1, corresponding to approximately 74 µl/ml. Thus, the EC50 probably lies between 74 and 100 µl/ml(14).

The EC50 range for low toxicity is defined as 60 to 600 µl/ml in Litton Bionetics' response to Technical Directive No. 301. According to this definition, the coke quench tower emission sample is of low toxicity(14).

TABLE 8-14

RESULTS OF MUTAGENICITY AND TOXICITY ASSAYS OF A COKE QUENCH TOWER EMISSION SAMPLE

	MUTAGENICITY (Results given in revertants per plate)								TOXICITY (Results given in population counts -10^6 dilution - per plate)			
Salmonella strains:	TA-1535		TA-1537		TA-98		TA-100		TA-1535	TA-1537	TA-98	TA-100
	1	2	1	2	1	2	1	2				
	Non Activation Tests											
Solvent Controls[a]	8	7	21	11	48	54	146	165	42	6	196	56
Positive Controls[b]	708	696	168	167	0	296	0	2,666	21	0	190	64
Mg/plate of sample:												
0.01000	6	7	19	20	45	67	145	158	19	16	55	70
0.10000	8	8	16	18	50	53	176	159	31	14	121	68
1.00000	10	7	16	16	54	49	168	133	40	22	167	68
10.00000	11	8	16	14	64	59	174	163	27	6	188	54
	Rat Liver Activation Tests											
Solvent Controls[a]	4	9	19	20	35	33	155	195	59	66	0	56
Positive Controls[b]	45	46	293	309	1,072	923	1,889	1,844	27	6	233	44
Mg/plate of sample:												
0.01000	3	7	16	15	41	31	215	171	43	36	210	86
0.10000	9	8	25	23	31	33	185	179	44	53	210	83
1.00000	8	3	25	15	31	19	185	178	39	46	231	67
10.00000	7	9	12	17	31	33	204	188	52	50	229	73

[a] Solvent used was dimethyl sulfoxide, 50 µl/plate

[b] Positive controls for each Salmonella strain were:

TA-1535, TA-100	N-Methyl, N-Nitro, N-Nitrosoguanidine	1 UG/Plate
TA-1537	9 - Aminoacridine	50 UG/Plate
TA-98	2 - Nitrofluorene	10 UG/Plate

Note: These data are the results of tests performed by Litton Bionetics.(14)

TABLE 8-15

RESULTS OF THE CHO CLONAL CYTOTOXICITY ASSAY OF A COKE QUENCH TOWER EMISSION SAMPLE: COLONY COUNTS AND PERCENT RELATIVE SURVIVAL

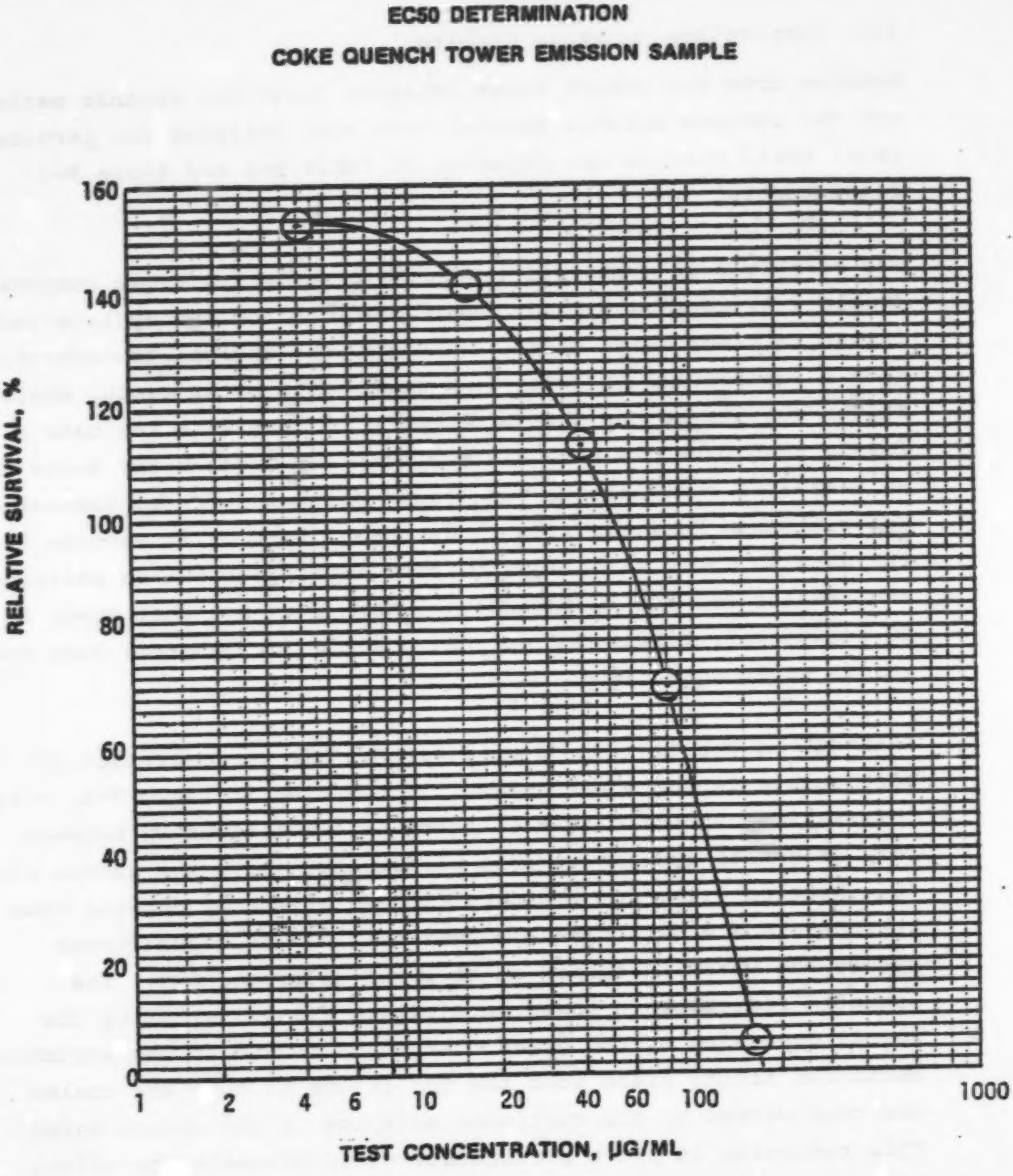
Sample	Applied Concentration µl/ml	Original Concentration[a] µl/ml	Colony Numbers				Relative Survival %	Cloning Efficiency %
			Dish #1	Dish #2	Dish #3	Avg		
Untreated Control	0	--	360	--	--	360	121.2	72.0
Solvent Control[b]	20	--	284	310	--	297	100.0	59.4
Test Material	0.5	4.0	573	454	339	455	153.2	--
Test Material	2.0	16.0	399	465	400	421	141.8	--
Test Material	5.0	40.0	355	345	308	336	113.1	--
Test Material	10.0	80.0	199	211	210	207	69.7	--
Test Material	20.0	160.0	12	19	20	17	5.7	--

[a] The original sample was concentrated 8-fold during the solvent exchange to DMSO.

[b] Solvent used was dimethyl sulfoxide.

Note: These data are the results of tests performed by Litton Bionetics.(14)

FIGURE 8-1



Note: This data analysis supplied by Litton Bionetics (14).

9.0 PARTICULATE EMISSIONS

9.1 Particulate Emission Results

Samples from the quench tower emission tests for organic matter and for benzene soluble residue were also analyzed for particulate; these results are reported in Table 9-1 and Table 9-2 respectively.

The breakdown of particulate results by sampling train component (Table 9-1) reveals similar concentrations for the cyclone and filter in clean water tests. However, the cyclone concentrations show a substantial increase in contaminated water tests, whereas filter concentrations show a decrease. These data indicate a fairly even particle size distribution for clean water tests and an increased concentration of larger particles for contaminated water tests. Particle size is discussed further in Section 9.2. The data in Table 9-1 also show that total particulate emissions are greater for the contaminated water tests and that there is no substantial difference in test results for nongreen coke tests versus green coke tests.

Although no correlation of greenness to the concentration of particulate in the stack aerosol is revealed in Table 9-1, visual observations indicate that 1) there is a relationship between coke greenness and the visible particulate above the quench car (see Section 6.1); and 2) there is a relationship between coke greenness and a dark haze observed exiting the quench tower before the water is turned on to a car of green coke. The dramatic reduction in tower particulate emissions during the actual quenching of the green coke might be due to the scrubbing mechanism taking place when the top layers of coke are cooled and then wetted by the continued spraying of the quench water. This reduction in plume particulate could minimize the effect of coke greenness on quench tower emissions.

Table 9-1

COKE QUENCH TOWER PARTICULATE EMISSIONS

Test No.	Coke	Cyclone		Nozzle/Probe		Filter		Total	
	Greenness (avg.)	mg/m^3	g/metric ton coal	mg/m^3	g/metric ton coal	mg/m^3	g/metric ton coal	mg/m^3	g/metric ton coal
Clean Water Tests									
7	1.2	445	382	279	240	405	348	1130	970
10	1.5	278	261	67	63.3	Negative		N/A	
9	1.6	220	209	98	93.5	Negative		N/A	
4	1.6	277	255	No Sample		457	420	N/A	
6	1.6	456	500	59	64.5	Negative		N/A	
8	1.8	306	261	64	55.0	345	295	716	611
11	3.2	194	198	63	64.1	27.0	27.7	283	290
3	3.3	275	311	28	31.8	355	400	659	743
2B	3.4	263	262	32	32	397	397	692	691
12	3.7	415	412	62	61.8	Negative		N/A	
5	4.0	412	377	35	31.8	360	330	807	739
Contaminated Water Tests									
16	0.3	962	924	61	58.8	167	160	1190	1140
15	0.5	891	874	123	120	202	197	1216	1190
17	0.5	633	710	89	100	178	200	901	1010
14	1.5	863	1040	89	108	59.0	71.0	1011	1220

"NA" = Not Available

"Negative" indicates a negative sample weight. It has been determined that this result is most likely due to holes in the filter which formed during sampling, allowing particulate to escape to the back half of the train. See Section 6.6 for a detailed discussion.

Table 9-2

BENZENE SOLUBLE RESIDUE TESTS

TOTAL PARTICULATE

Benzene insoluble particulate determined for each test is added to the benzene soluble residue to yield total particulate.

SAMPLE	mg/m^3	g/metric ton of coal
Test No. 1 - clean,3*		
cyclone	236	262
nozzle/probe	38.2	42.4
filter	3.95	4.35
condenser	34.6	38.2
adsorber	155	172
Total	468	519
Test No. 2 - clean, 1.8		
cyclone	219	301
nozzle/probe	22.8	31.3
**filter	no sample	
***condenser	146	201
adsorber	129	177
Total	517	710
Test No. 13 - contaminated, 1.5		
cyclone	434	424
nozzle/probe	33.7	33.1
filter	38.7	38.0
condenser	349	342
adsorber	160	157
Total	1015	994

* Quench water quality, coke greenness

** Filter burned during test

*** This benzene soluble sample appeared contaminated

TABLE 9-3

PARTICULATE EMISSION SUMMARY

Organic Emission Tests

Sampling Train Component: average (range)	CLEAN QUENCH WATER[a] Nongreen Coke (Tests 7,8) mg/m^3	CLEAN QUENCH WATER[a] Nongreen Coke (Tests 7,8) kg/metric ton coal	CLEAN QUENCH WATER[a] Green Coke (Tests 2B,3,5,11) mg/m^3	CLEAN QUENCH WATER[a] Green Coke (Tests 2B,3,5,11) kg/metric ton coal	CONTAMINATED QUENCH WATER Nongreen Coke (Tests 14-16) mg/m^3	CONTAMINATED QUENCH WATER Nongreen Coke (Tests 14-16) kg/metric ton coal	CONTAMINATED QUENCH WATER Green Coke (No Tests) mg/m^3	CONTAMINATED QUENCH WATER Green Coke (No Tests) kg/metric ton coal
Cyclone (20μm, 50% cut size)	380 (310-450)	0.32 (0.26-0.38)	230 (190-410)	0.29 (0.20-0.41)	840 (630-960)	0.89 (0.71-1.04)	-	-
Probe/Nozzle	170 (64-280)	0.15 (0.055-0.24)	40 (32-63)	0.039 (0.032-0.064)	91 (61-120)	0.10 (0.059-0.12)	- -	- -
Filter	370 (350-410)	0.32 (0.30-0.35)	280 (27-400)	0.29 (0.027-0.40)	150 (59-200)	0.16 (0.071-0.20)	-	-
Total Front Half	920 (720-1100)	0.79 (0.61-0.97)	610 (280-810)	0.62 (0.29-0.74)	1080 (900-1200)	1.1 (1.0-1.2)	-	-

	Total (Tests 2B,3,5,7,8,11) mg/m^3	Total (Tests 2B,3,5,7,8,11) kg/metric ton coal	Total (Tests 14-17) mg/m^3	Total (Tests 14-17) kg/metric ton coal
Cyclone (20μm, 50% cut size)	320 (190-450)	0.30 (0.20-0.50)	840 (630-960)	0.89 (0.71-1.0)
Probe/Nozzle	84 (28-280)	0.075 (0.032-0.24)	91 (61-120)	0.10 (0.059-0.12)
Filter	320 (27-400)	0.30 (0.027-0.42)	150 (59-200)	0.16 (0.071-0.20)
Total Front Half	720 (280-1100)	0.68 (0.29-0.97)	1080 (900-1200)	1.2 (1.0-1.2)

Benzene Soluble Residue Tests

	CLEAN WATER - GREEN COKE (Test 1)[b] mg/m^3	CLEAN WATER - GREEN COKE (Test 1)[b] kg/metric ton coal	CONTAMINATED WATER - NONGREEN COKE (Test 13) mg/m^3	CONTAMINATED WATER - NONGREEN COKE (Test 13) kg/metric ton coal
Cyclone (20μm 50% cut size)	240	0.26	430	0.42
Probe/Nozzle	38	0.042	34	0.033
Filter	4.0	0.0044	39	0.038
Subtotal - Front Half	280	0.31	500	0.49
Total (including front half condenser, adsorber)	470	0.52	1020	0.99

---

[a] Sampling train components for some tests (4,6,9,10,12) have negative results or no sample (see Table 9-1). Results for these tests were not incorporated into this summary. No major difference occurs in the average values when this procedure is used.

[b] Test No. 2 was not included in these summary results since there was no filter sample and the condenser sample appeared contaminated.

Particulate data from the benzene soluble residue tests (Table 9-2) were obtained by adding the benzene insoluble particulate results to the benzene soluble residue (reported in Table 8-10). In addition to the front half (cyclone, nozzle/probe, and filter) the condenser and adsorber were also analyzed for each test.

A summary of all the particulate data is presented in Table 9-3. Considering the organic tests, the clean water-nongreen coke tests average 0.79 kg/metric ton of coal and the clean water - green coke tests average 0.62 kg/metric ton of coal. The clean water tests average 0.68 kg/metric ton of coal and the contaminated water tests, 1.1 kg/metric ton of coal. Again, there is a substantial increase in particulate concentration for contaminated water tests, but no notable difference in results for green versus nongreen coke tests. The benzene soluble residue tests show only half the concentration of front half particulate found in the organic tests.

9.2 Particle Size

Some important aspects of the size distribution of particulate in coke quench tower emissions are revealed in Table 9-3. The sampling train provides a breakdown of particle size. The cyclone was designed to capture aerosols generally large enough to be easily visible - the 50% cut size was about 20 micrometers. The D_{50} cut size of the "in-stack" cyclones at test conditions was calculated for each test as shown in Table 9-4, Column 11.

The D_{50} cut size of any given cyclone is determined by a number of variables. These variables include gas density, gas viscosity, gas inlet velocity, particle density, and particle size and shape. The value of the gas density is so small relative to particle density that, in most cases, variation in gas density will have a negligible effect on cyclone separation efficiency or calibration. For a given set of conditions in which particle density, gas density, and gas viscosity are assumed to be fixed,

TABLE 9-4

CUT SIZE OF "IN STACK" CYCLONE AT TEST CONDITIONS

	TEST TIME/MIN	GAS			WATER	VOL. OF MIXTURE DRY GAS AND IMPINGER WATER AT STACK TEMP.				CYCLONE
TEST NUMBER (1)	CAR IN CAR OUT (2)	DSCF PER TEST PERIOD (METER DATA) (3)	STACK TEMPERATURE °F (4)	LBS DRY GAS DURING TEST PERIOD (5)	VOLUME OF VAPOR CONDENSED (ml) (6)	LBS H_2O/LBS DRY GAS IN SAMPLE AFTER CYCLONE (7)	ACF PER POUND (8)	ACF (9)	FLOW OF MIXTURE ACFM (10)	D_{50} CUT SIZE MICRONS (11)
1	12.3	20.78	175	1.56	102.5	0.14	19.6	30.6	2.5	11
2	14.3	27.65	175	2.07	237.6	0.25	22.4	46.4	3.2	10
2B	12.1	9.7	175	0.73	75.6	0.23	21.8	15.9	1.3	24
3	11.6	10.41	175	0.78	54.3	0.15	19.8	15.4	1.3	24
4	12.1	7.95	175	0.60	39.8	0.15	19.8	11.9	1.0	30
5	12.9	10.17	175	0.76	74.4	0.22	21.6	16.4	1.3	24
6	11.9	10.69	175	0.80	73.1	0.20	21.1	16.9	1.4	22
7	12.4	9.67	175	0.72	52.1	0.16	20.3	14.6	1.2	26
8	9.4	9.96	175	0.75	107.6	0.32	23.7	17.8	1.9	16
9	12.1	10.30	175	0.77	116.9	0.33	23.8	18.3	1.5	21
10	9.6	9.11	175	0.68	59.9	0.19	20.6	14.0	1.4	22
11	10.4	10.43	175	0.78	41.7	0.12	18.7	14.6	1.4	22
12	8.2	7.15	175	0.54	67.7	0.28	22.5	12.1	1.5	21
							Clean Test Average			18
13	14.8	12.28	175	0.92	82.2	0.20	21.1	19.4	1.3	24
14	13.5	12.47	175	0.93	56.7	0.13	19.5	18.1	1.3	24
15	9.7	8.74	175	0.66	64.2	0.21	21.3	14.1	1.5	21
16	9.7	9.56	175	0.72	76.7	0.23	21.8	15.7	1.6	20
17	15.8	13.77	175	1.03	90.8	0.19	20.6	21.2	2.2	15
							Contaminated Test Average			21

the D_{50} cut size of a given cyclone is determined largely by the gas inlet velocity and the particle size and shape.(19)

Calibration data for this series of cyclones has been utilized to construct Figure 9-1. This graph relates sample flow rate in actual cubic feet per minute to the D_{50} cut size in micrometers. ACFM is, in this case, used as a convenient indication of inlet gas velocity. It is an average value based on the measured amount of dry gas recorded by the dry gas meter (Table 9-4, Column 3), the elapsed time of the test (Table 9-4, Column 2), and the volume of water vapor. These values are corrected to actual stack conditions at the temperature of the test (Table 9-4, Column 4). Following the determination in ACFM of the gas flow for each test (Table 9-4, Column 10), the D_{50} cut size in micrometers is read from Figure 9-1. Since the inlet velocity was an average, the D_{50} cut size is also an average.

In the following example, the D_{50} cut size is determined for Test 4:

Example

7.95 dscf x 0.07495 lbs/cf = 0.60 lbs dry gas during test period.

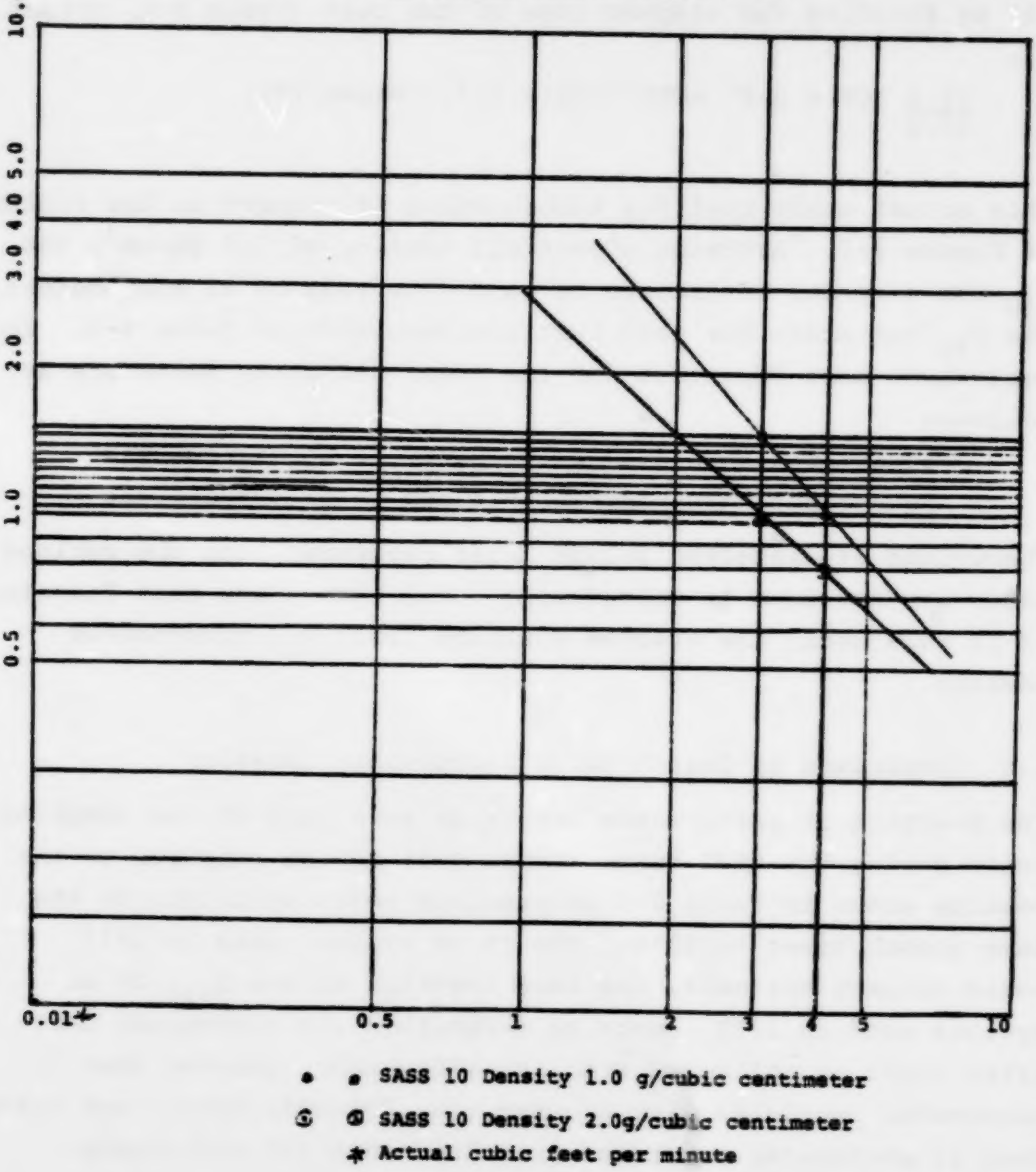
The volume of water vapor condensed and collected in the impinger and the condenser (Table 9-4, Column 6) is converted to pounds of water vapor per pound of dry gas (Table 4, Column 7) as follows:

$$\frac{39.8 \text{ ml } H_2O}{454 \text{ ml/lb } H_2O \times 0.60 \text{ lbs dry gas}} = 0.15 \text{ lbs water/lb dry gas}$$

This value (the absolute humidity) is used with a reference table (20) to determine the ACF/lb of the mixture of dry gas and water vapor. The water droplets collected in the cyclone is not included in these calculations.

Figure 9-1

D_{50} Cut point in micrometers vs cubic feet per minute for cyclone used in sample train



ACF per pound (Table 9-4, Column 8) is converted to ACF (Table 9-4, Column 9):

$$19.8 \text{ ACF/lb} \times 0.60 = 11.8 \text{ ACF}$$

ACF of mixture is converted to ACF per minute (Table 9-4, Column 10) by dividing the elapsed time of the test (Table 9-4, Column 2):

$$\frac{11.8}{12.1} \text{ ACF} = 0.97 \text{ ACFM (Table 9-4, Column 10).}$$

This actual cubic feet per minute value is entered on the ordinate of Figure 9-1. Assuming a particle density of 2.0 gm/cm^3, the D_{50} cut size for conditions of test 4 is read as 32 micrometers. The D_{50} cut sizes for each test are tabulated in Table 9-4. The equivalent mass diameters for the clean and dirty tests are as follows:

Equivalent mass diameter - Dirty	21 micrometers
Equivalent mass diameter - clean	18 micrometers

The weight of dissolved solids later recovered from the cyclone water was not used in calculating these equivalent mass diameters. If it were used, the average would be about 0.5 micrometers smaller.

9.3 Comparison of Quench Tower Particulate Emission

The fraction of particulate caught in each part of the sampling train during the 1977 tests (Table 9-3) may be compared to the results shown in Table 9-5 of previous tests at Lorain on the same quench tower in 1976. The 10 μm cyclone used in 1977 would collect basically the same fraction as the D_{50}, 20 μm cyclone used in 1977, since by definition, 10 micrometer particles would be collected with 50% efficiency, greater than 10 micrometer particles with greater than 50% efficiency, and less than 10 micrometer particles with less than 50% efficiency. Only the 10 micrometer to 20 micrometer particles would not have been as efficiently collected in the 1977 tests. Since the cyclone collection was greater in 1977, any difference in

TABLE 9-5

QUENCH TOWER PARTICULATE EMISSIONS U.S. STEEL CORPORATION LORAIN WORKS QUENCH TOWER NO. 1 - NOVEMBER 1976[(1)]

Sampling Train Component	Clean Make-up Water (13 Test Runs) Kg/metric ton of coal Average (range)	Contaminated Make-up Water (12 Test Runs) Kg/metric ton of coal Average (range)
Cyclone (10 micrometers, 50% cut size)	0.14 (0.048-0.027)	0.59 (0.34-0.84)
Probe	0.58 (0.15-0.90)	0.58 (0.24-1.2)
Filter (99.99% efficiency for particles 0.3 micrometers and larger)	0.0075 (0-0.037)	0.23 (0.15-0.37)
Front half of sampling train catch	0.73 (0.34-1.0)	1.4 (0.87-2.2)
Back half of sampling train catch	0.080 (0.025-0.16)	0.40 (0.18-0.88)
Total Quench Tower Particulate Emissions	0.81 (0.38-1.2)	1.8 (1.1-3.0)

particle collection due to this fraction would be relatively minimal. The fact that the total amount of particulate collected in the cyclone was greater than in 1976 could have been the result of the increase in the open area in the center of the baffles (see Table 9-7).

The total front half of the sampling train catch in the 1977 tests is very similar to the 1976 results. Again there was a dramatic decrease in the emissions when clean water was used rather than contaminated water. However, the distribution of size fractions as collected in different parts of the train is somewhat different from that in the 1976 tests. The weight of larger aerosols collected by the initial cyclone in 1977 was about 45% of the total weight emitted when quenching with clean water and about 75% of the contaminated water quench emission. The average size of the particulate in the plume aerosol was less than 4 micrometers in the 1976 tests but this would be shifted towards a larger size in the 1977 Lorain tests due to the greater cyclone collection.

The results of tests at a Canadian plant(17) (Table 9-6) indicate that the particulate per ton of coal in the Canadian tests was about 20% of that found during the 1977 Lorain tests. The large size fraction caught in the cyclone during the 1977 Lorain test (larger than 20 micrometers) was about 12 times as much as in Canada. This would be expected considering the open area in the Lorain baffles. The amount caught in the probe nozzle and condenser at Lorain was about the same as that caught in the probe and nozzle during the Canadian tests. When compared to the Canadian tests which used clean water for makeup, the amount of particulate caught on the filter was 12 times greater during the organic matter tests at Lorain using clean water as makeup.

TABLE 9-6

QUENCH TOWER PARTICULATE EMISSIONS
DOMINION FOUNDRIES AND STEEL, LTD.

AUGUST 1977(21)

Sampling Train Component	"Clean" Make-up Water (9 Test Runs) Kg/metric ton of coal
Cyclone (10 micrometers, 50% cut size)	0.025 (0.0050 - 0.075)
Probe	0.090 (0.060 - 0.13)
Filter (99.99% efficiency for particles 0.3 micrometers and larger)	0.025 (0.015 - 0.060)
Front half of sampling train catch	0.140 (0.095 - 0.20)
Back half of sampling train catch	0.10 (0.055 - 0.19)
Tower Quench Tower Particulate Emissions	0.24 (0.16 - 0.31)

9.4 Baffles

Quench tower No. 1 at Lorain was equipped with baffles (Figure 9-2) as described in Figures 9-3 and 9-4 which were based on U.S. Steel Drawing No. LA-100891[(1)]. These figures were somewhat modified however, as described below.

As can be seen in Figure 9-4 the baffles were constructed in such a way as to allow a vertical area of one inch between the bottom of one baffle and the top of another. This verticle open area allowed a substantial portion of the stack flow to pass straight through the baffles with little opportunity for even larger size particles to impinge on the baffle surfaces.

Several baffles had been removed and this provided additional open area. The U.S. Steel drawing calls for 11 slanted boards in each baffle section (See Figure 9-3) but only 10 full boards in 5 of the sections and 6 full boards in one section were actually in place (Figure 9-5) at the time of the test. The effect of these open areas would be to reduce the resistance to gas flow and increase the draft up the tower. There were come charred remains which indicated some of these baffles had been burned out. The effect of removing baffles was to increase the vertical open area as can be seen in Table 9-7 which compares the open area of the baffled section in 1976 and 1977.

FIGURE 9-2
BAFFLED SECTION OF QUENCH TOWER

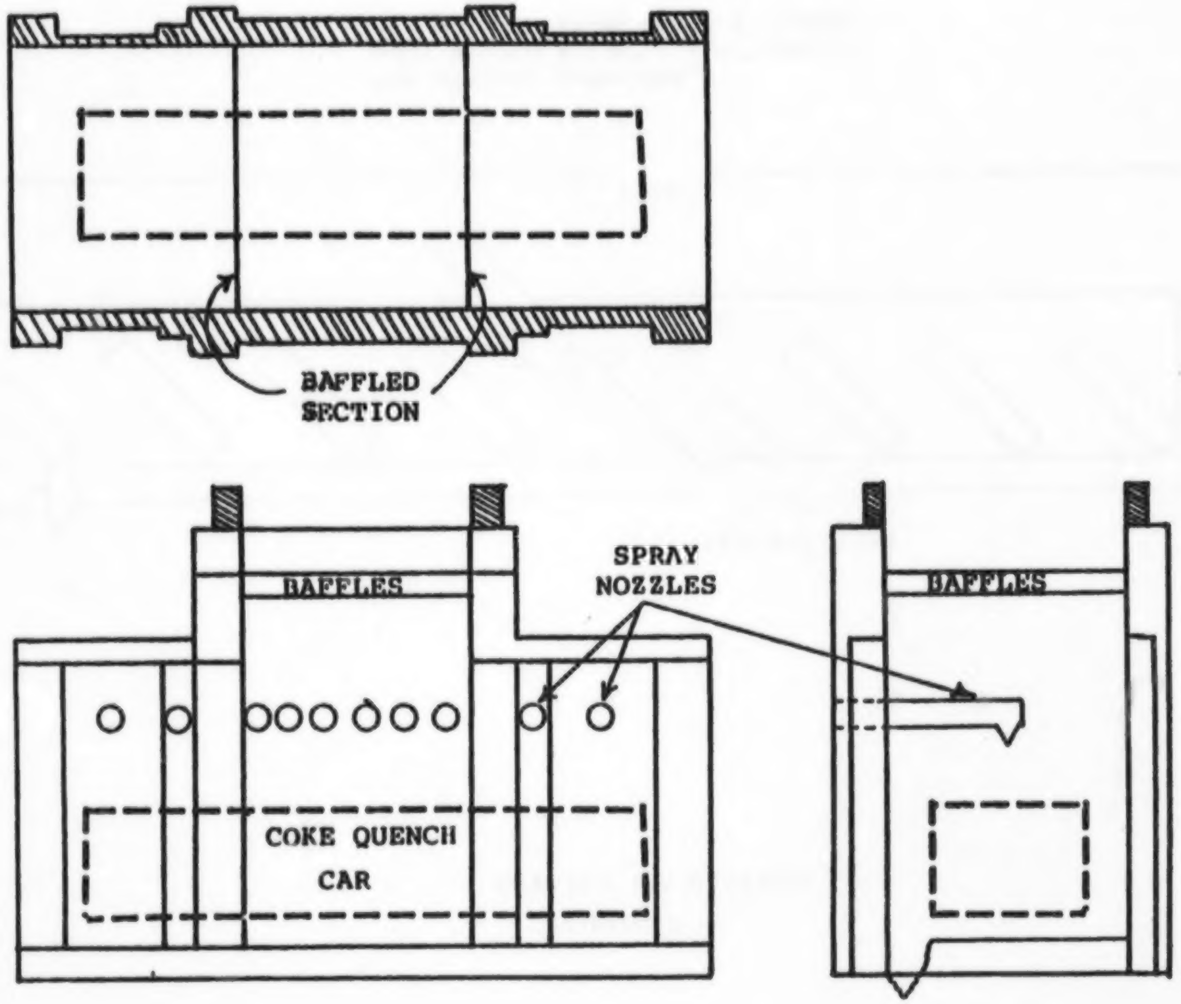
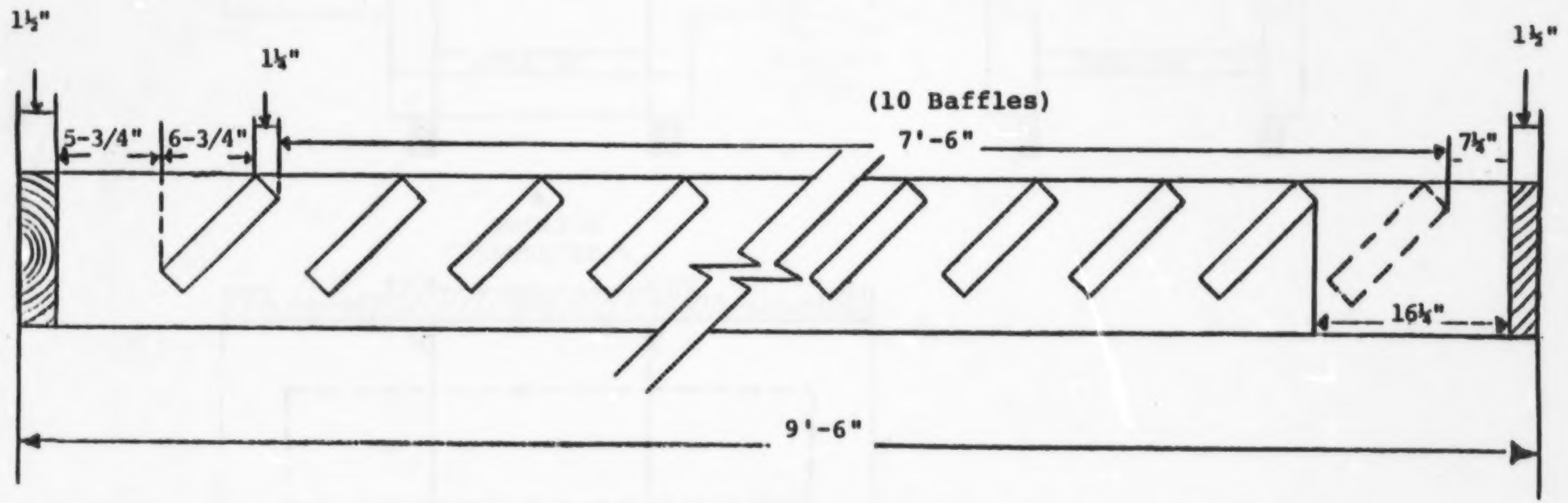

BAFFLED
SECTION
BAFFLES
SPRAY
NOZZLES
BAFFLES
COKE QUENCH
CAR

Figure 9-3
DETAILS OF BAFFLES


1½"
1¼"
1½"
(10 Baffles)
5-3/4"
6-3/4"
7'-6"
7¼"
16¼"
9'-6"

Six sections installed
each section 6'-3½" x 9'-0" overall
6'-0½" x 9'-3" inside

FIGURE 9-4

OPEN AREA BETWEEN BAFFLES

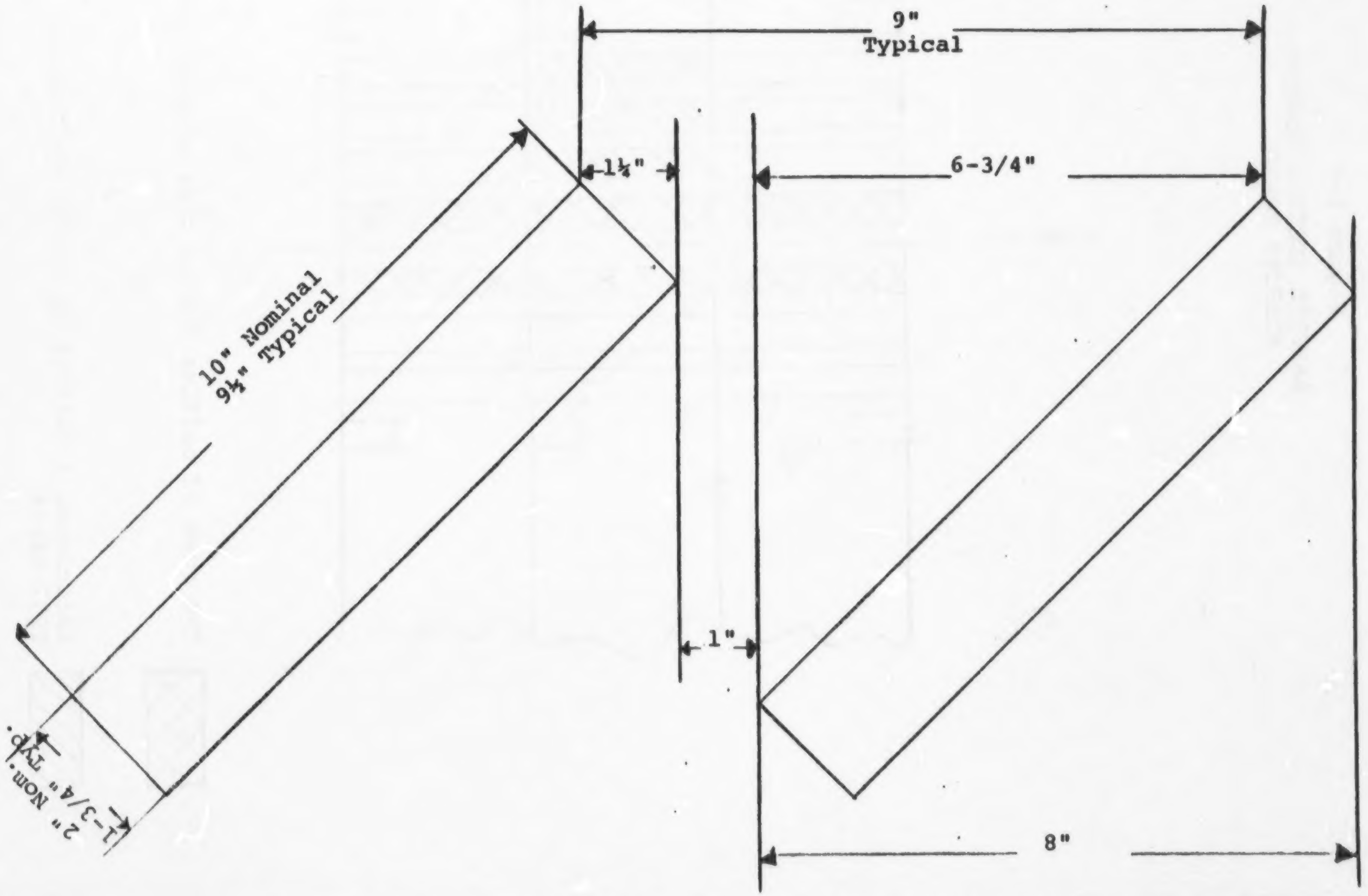
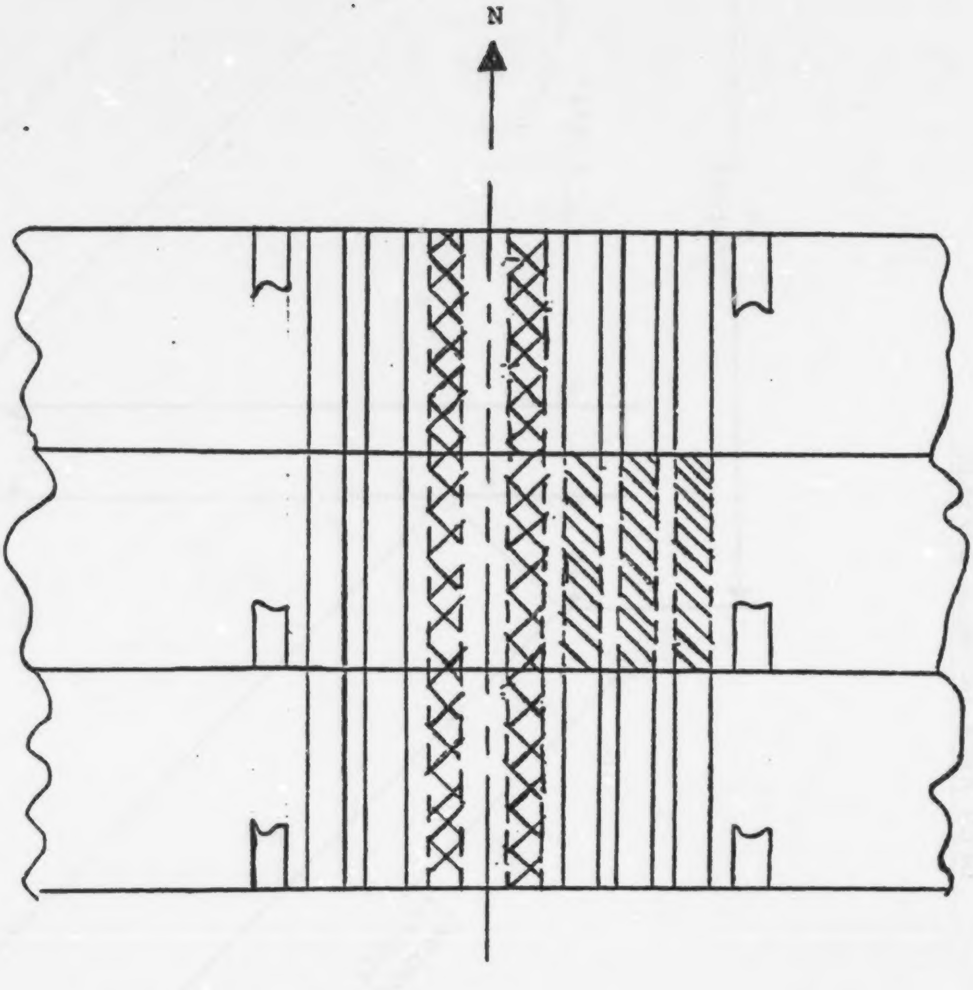

9"
Typical
1¼"
6-3/4"
10" Nominal
9¼" Typical
1"
2" Nom.
1-3/4" Typ.
8"

Figure 9-5

BAFFLED SECTION SHOWING
MISSING BOARDS



▦ Two rows of baffles out at time of 1976 tests

▨ Additional 3 baffles in center section out at time of 1977 tests

Six sections designed for 11 baffles each

TABLE 9-7

BAFFLE OPEN AREA

		Square feet	Open area as a % of total area
Total open area of the tower before any baffles were installed from Dwg. LA-100891 (U.S.S. Corp.) 19' - 2" x 19' - 2"		367	100
Total vertical open area of the tower after the baffles were installed. Based on U.S. Steel Corp. Dwg.LA-100891- 11 rows of baffles in each section		70	19
Total vertical open area with 10 rows of baffles in 5 sections and 6 rows in one section as actually installed at time of test program		106	29
Open area in center of tower due to Omission of baffles	1976	24	6
	1977	36	10

The efficiency of these baffles and more detailed discussion is to be found in the report of the 1976 test series(1).

10.0 QUENCH WATER ORGANICS AND WATER FLOW

10.1 Organics in Quench Water

The amounts of organic species detected by GC/MS in the quench water (both the inlet of the spray nozzles and makeup to the sump) are given in Tables 10-1 and 10-2.

The flushing liquor used as makeup during the contaminated water tests contained almost all of the species eventually found in the stack emission. However, as molecular weight increases the ratio of the quantity of species in the stack emission to the quantity introduced in the makeup liquor becomes less and less. The lower the molecular weight the higher the boiling point; therefore, the lower molecular weight species are readily stripped from the quench water by the evaporation and distillation process of the quench. The same relationship is also apparent when comparing the quantity of each organic species introduced to the quench system by the makeup liquor and the quantity of each species available from the inlet water which was being used repeatedly to quench the coke. As would be expected, the inlet water is stripped of lower molecular weight species and the higher molecular weight species tend to remain in the quench water. A few of these higher molecular weight compounds do not even appear in the stack emissions. There is no sharp cut off due to the high temperature of the uncooled portions of incandescent coke and the stripping action of the steam which tends to lower the boiling point of the higher molecular weight compounds.

In the case of the clean quench water samples only a small quantity of organics was found. The organic matter in the stack emissions from clean tests could come from a number of sources including the sludge in the sump (where organics from previously used flushing liquor could collect) or the more likely possibility that organics from the coke itself are released during the quenching process and become part of the quench tower emission.

TABLE 10-1

QUENCH WATER ANALYSIS

(in μg/l)

POLYCYCLIC AROMATIC HYDROCARBONS

Species	Clean Water		Contaminated Water	
	Service Water	Inlet to Nozzle	Flushing Liquor	Inlet to Nozzle
Indeno				4.82
Naphthalene	3.09	5.86	8,240	>2,240
Benzothiophene			1,270	162
Methyl Naphthalenes			1,610	216
Acenaphthylene/Biphenylene	0.275	1.59	3,080	668
Biphenyl	1.04	1.47	242	33.1
Dimethyl Naphthalenes			233	35.8
Fluorene			1,670	394
Carbazole			1,320	1,610
Dibenzofuran/methyl biphenyl			994	193
Anthracene/phenanthrene	85.6	11.1	4,230	1,380
Dibenzothiophene			194	44.9
Methyl anthracenes	39.8	4.09	310	111
Fluoranthene	1.92	9.48	1,270	692
Pyrene	3.03	13.9	801	675
$C_{16}H_{12}PAH$				4.49
$C_{16}H_{12}PAH$				16.6
$C_{16}H_{12}PAH$				4.29
$C_{16}H_{16}PAH$				10.3
Methyl Fluoranthene & Methyl Pyrene			324	150
Dihydrobenzofluorene				
Chrysene/Benz(a)anthracenes		6.27	569	295
Naphthobenzothiophene				37.4
Methyl-chrysenes			85.7	54.6
Benzofluoranthene, benzo(e)pyrene & Benzo(a)pyrene			400	259
Perylene			483	364
7,12 Dimethyl Benz(a)anthracene			0.589	
Methyl-benzo pyrenes			79.0	74.8
Dibenzo(c,g)carbazole				
3-methyl cholanthrene			17.1	
Indeno(1,2,3-cd)pyrene			39.1	79.8
Benzo(ghi)perylene			126	244
Dibenzo(a,h)anthracene				
Coronene			27.9	38.9
Dibenzo(ai & ah)pyrenes				70.0
Total	135	53.8	27,600	10,200
Benzo(a)pyrene		27	300	440

POLAR COMPOUNDS

Polar Compounds	Clean Water		Contaminated Water	
	Service Water	Inlet to Nozzle	Flushing Liquor	Inlet to Nozzle
Pyridine	1.14		7,880	134
Methyl Pyridine	1.14		4,700	1,510
Aniline			3,000	888
Phenol			2,770	2,250
Benzonitrile			3,080	866
Dimethyl/ethyl pyridine	0.762		8,200	1,420
Toluidine			2,060	175
Cresol			1,410	122,000
Indole			13,500	22,900
Trimethyl pyridine			1,560	338
Methyl cresol				
Quinoline			23,400	10,600
Isoquinoline			6,900	7,090
Trimethyl phenol				
Methyl quinoline			1,980	1,040
*Phthalates		>1,660	>2,380	>1,620
Dimethyl/ethyl quinoline			93.3	87.5
Acridine			745	531

* Phthalates are considered to be a contaminant.

** These values for benzo(a)pyrene were determined by a special analysis with high sensitivity for BaP.

All blanks indicate that the concentration of the species was below the detection level. The detection limit for each PAH species varies with molecular weight, reaching differences from five to twenty times with a lower limit at naphthalene and a higher limit at coronene. This "upper limit" for each test is as follows:

	Clean Water		Contaminated Water	
	Service Water	Inlet to Nozzle	Flushing Liquor	Inlet to Nozzle
Detection Limit in μg/l	≤48	≤66	≤110	≤56

TABLE 10-2

QUENCH WATER ANALYSIS

(in grams/metric ton of coal)

POLYCYCLIC AROMATIC HYDROCARBONS

	Clean Water		Contaminated Water	
Species	Service Water	Inlet to Nozzle	Flushing Liquor	Inlet to Nozzle
Indene				0.00291
Naphthalene	0.00187	0.00354	4.98	>1.36
Benzothiophene			0.765	0.0980
Methyl Naphthalenes			0.975	0.131
Acenaphthylene/Biphenylene	0.000166	0.000960	1.86	0.404
Biphenyl	0.000630	0.000890	0.146	0.0200
Dimethyl Naphthalenes			0.141	0.0216
Fluorene			1.01	0.238
Carbazole			0.800	0.970
Dibenzofuran/methyl biphenyl			0.600	0.117
Anthracene/phenanthrene	0.0515	0.00670	2.56	0.835
Dibenzothiophene			0.117	0.0271
Methyl anthracenes	0.0241	0.00247	0.187	0.0670
Fluoranthene	0.00116	0.00575	0.765	0.418
Pyrene	0.00183	0.00840	0.485	0.408
$C_{16}H_{12}$PAH				0.00271
$C_{16}H_{12}$PAH				0.0100
$C_{16}H_{12}$PAH				0.00259
$C_{16}H_{16}$PAH				0.00620
Methyl Fluoranthene and Methyl Pyrene			0.196	0.0905
Dihydrobenzofluorene				
Chrysene/Benzo(a)anthracenes		0.00379	0.344	0.178
Naphthobenzothiophene				0.0226
Methyl-chrysenes			0.0520	0.0330
Benzofluoranthene, Benzo(e)pyrene and Benzo(a)pyrene			0.242	0.157
Perylene			0.292	0.220
7,12 Dimethyl Benz(a)anthracenes			0.000356	
Methyl-benzo Pyrenes			0.0477	0.0452
Dibenzo(c,g)carbazole				
3-methyl cholanthrene			0.01035	
Indeno (1,2,3)-cd pyrene			0.0237	0.0482
Benzo(ghi)perylene			0.0760	0.148
Dibenzo(ah)anthracene				
Coronene			0.0169	0.0235
Dibenzo(ai & ah)pyrenes				0.00423
Total PAH	0.0810	0.0325	16.7	6.10
Benzo(a)pyrene**		0.0161	0.181	0.267

POLAR COMPOUNDS

	Clean Water		Contaminated Water	
Species	Service Water	Inlet to Nozzle	Flushing Liquor	Inlet to Nozzle
Pyridine	0.000685		4.77	0.0810
Methyl Pyridine	0.000685		2.84	0.910
Aniline			1.81	0.540
Phenol			1.67	1.36
Benzonitrile			1.86	0.523
Dimethyl/ethyl pyridine	0.000462		4.96	0.860
Toluidine			1.24	0.106
Cresol			0.850	73.5
Indole			8.15	13.9
Trimethyl pyridine			0.945	0.204
Methyl Cresol				
Quinoline			14.1	6.40
Isoquiniline			4.16	4.28
Trimethyl phenol				
Methyl quinoline			1.19	0.630
Phthalates*		>1.00	>1.44	>0.980
Dimethyl/ethyl quinoline			0.0565	0.053
Acridine			0.450	0.321

* Phthlates are considered to be a contaminant.

** These values for benzo(a)pyrene were determined by a special analysis with high sensitivity for BaP.

All blanks indicate that the concentration of the species was below the detection level.

7192 liters (1900 gallons) of make-up water were added to the sump per quench. Therefore, 7192 liters were used as the basis for converting these values from mg/liter to g/metric ton of coal.

TABLE 10-3
RESULTS OF T.O.C. ANALYSIS OF WATER SAMPLES

Clean Water

MAKEUP			INLET		
DATE	SAMPLE IDENTIFICATION	PPM	DATE	SAMPLE IDENTIFICATION	PPM
11/9/77	13819	26	11/9/77	13814	30
11/9/77	13820	26	11/9/77	13815	18
11/9/77	13821	28	11/9/77	13816	25
11/9/77	13822	23	11/9/77	13824	28
11/19/77	20222	28	11/9/77	13825	27
11/19/77	20223	29	11/9/77	13826	25
11/19/77	20224	28	11/9/77	13827	27
11/19/77	20225	30			
	1977 Average =	27		1977 Average =	26
	Range =	(23-30)		Range =	(18-30)
	1976 Lorain Test Average	3.8		1977 Lorain Test Average	9.6

Contaminated Water

DATE	SAMPLE IDENTIFICATION	PPM	DATE	SAMPLE IDENTIFICATION	PPM
11/16/77	20202	2,200.0	11/16/77	20207	1,510.0
11/16/77	20203	2,422.0	11/16/77	20208	1,547.0
11/16/77	20204	2,317.0	11/16/77	20209	1,545.0
11/16/77	20205	2,130.0	11/16/77	20210	1,507.0
11/19/77	20217	2,282.0	11/19/77	20212	1,198.0
11/19/77	20218	2,088.0	11/19/77	20213	1,195.0
11/19/77	20219	2,252.0	11/19/77	20214	1,197.0
	1977 Average =	2,242		1977 Average =	1,386
	Range =	(2,088-2,422,		Range =	(1,195-1,547)
	1976 Lorain Test Average =	1,195		1976 Lorain Test Average =	1,098

The total organic carbon found in quench water samples averaged 27 ppm in clean makeup water and 2,242 ppm in contaminated makeup water. The average for clean inlet water was 26 ppm and for contaminated inlet water it was 1,386 ppm. The results of the TOC analysis are given in Table 10-3. As noted in the Table, these test results are comparable to those for the 1976 tests at Lorain(1).

10.2 Quench Water Flow

Water flow quantities at quench tower No. 1, U.S. Steel Co. Lorain Works were identified during EPA tests in 1976 and are presented in Table 10-4.

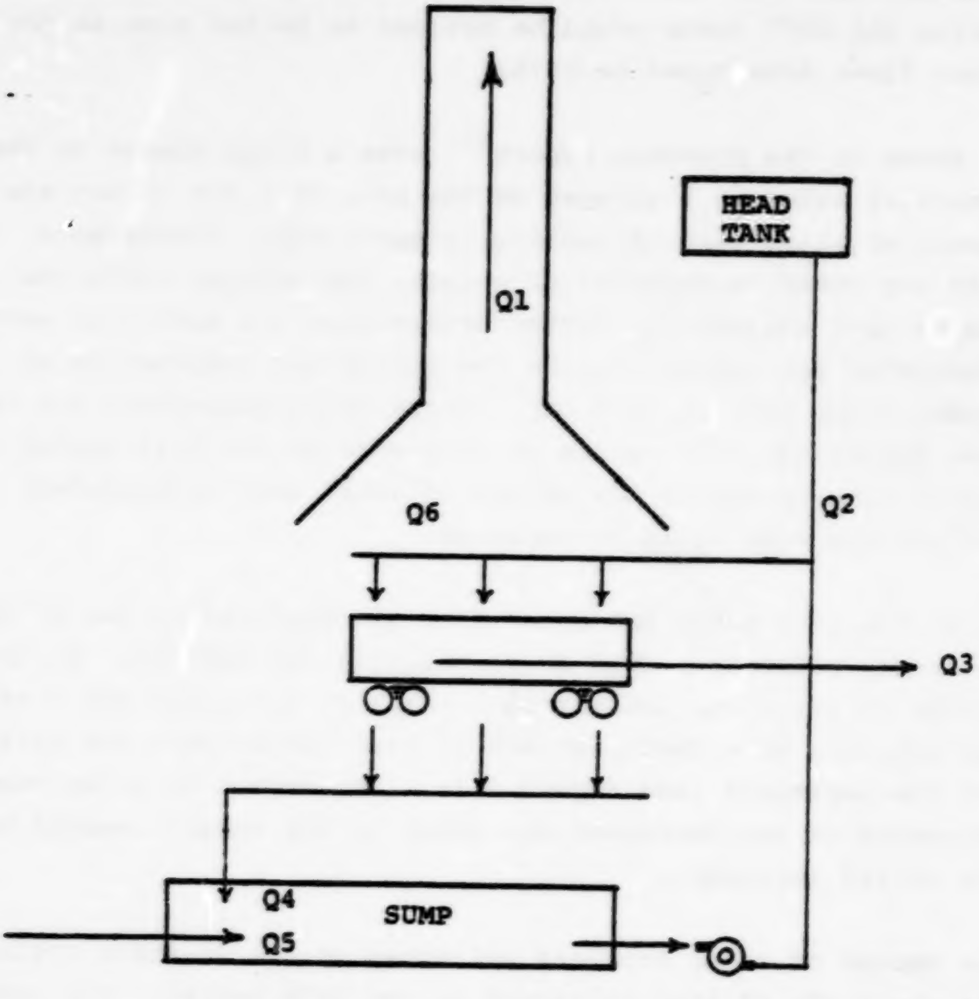
TABLE 10-4 WATER FLOW
(gals/quench)

Description	Identifier[a]	Min.	Max.	Avg.
Stack Flow	Q1	900	2500	1800
Inlet to Nozzle (Sprayed on Coke)	Q2	8100	10500	9200
Losses - retained by coke - car drainage - evaporation	Q3	NA	NA	150
Return to sump	Q4	NA	NA	7300
Make up to sump	Q5	NA	NA	1900
Moisture in Induced Air	Q6	7	50	20

[a] See Figure 10-1

The flow identifiers (Q1 to Q6) are used to describe the water flow into the quench tower process in Table 10-4 and Figure 10-1. During the 1976 tests, certain water flows such as Q_1 and Q_2 were measured, while others such as Q_4, Q_5 and Q_6 were calculated. Q_3 was an estimated value. The reliability of the quantities shown in Table 10-4 was reinforced by thermodynamic considerations.(1)

FIGURE 10-1
WATER BALANCE


Q1
HEAD TANK
Q6
Q2
Q3
Q4
SUMP
Q5

Q_1 = Stack Flow

Q_2 = Inlet to Nozzles

Q_3 = Losses

Q_4 = Return to Sump

Q_5 = Makeup to Sump

Q_6 = Moisture in Induced Air

No actual water flows were measured during the 1977 series. After reviewing the engineering aspects of the quench water system (there was no significant change in the equipment during the period November 1976 to November 1977) and in view of the thermodynamics involved it was concluded that the water flows during the 1977 tests could be assumed to be the same as the water flows determined in 1976.

As shown in the previous report(1) even a major change in the amount of water (Q_2) sprayed on the coke will not affect the amount of water used in cooling (evaporated). Furthermore, with any given arrangement of nozzles and storage tanks the single most influential factor determining the amount of water evaporated per quench will be the amount and temperature of incandescent coke in each car. Since these parameters are the same during the 1977 series as they were in the 1976 series no significant change in the amount of water used (evaporated) in cooling the coke would be expected.

As in the 1976 tests the stack flow was measured as one of the necessary parameters used in calculating isokinetics. In this series of tests the EPA Method 5 sampling train was modified by the addition of a condenser and an adsorber between the filter and the impingers (see Figure 6-7). The amount of water vapor recovered in the condenser was added to the amount removed by the cooled impingers.

The amount of water droplets collected in the in-stack cyclone was about 60% of that collected in the 1976 series. The average velocity of the stack flow was 23.6 fps in the 1977 series of tests which is 76% of the 30.9 fps average during the 1976 tests.(1) This lower velocity would entrain fewer and smaller drops from the baffles and the quenching area. The amount of water vapor (the amount collected in the condenser, the impinger and the silica gel) was 58% of that found in the 1976 test.

The detailed up-stack water flow (at test point B1) is presented in Table 10-5. This information is included for comparison purposes. However, for the mass balance of organic materials the 1976 water flow data will be used. The 1977 test series was run at one test position (B1, See Figure 6-9) and would not be as representative of the total stack flow as would the 1976 series. The 1976 tests were designed to provide an average of all stack flow parameters across the cross section of the tower.

The following calculation shows how Table 10-5 was constructed: Taking Test No. 1 (which consisted of five separate quenches) as an example:

34	ml of water caught in the cyclone (water drops)
50	ml of water caught in the condenser
36	ml of water caught in the impinger
17	ml of water caught in the silica gel
137	ml of water as vapor

A total of 137 ml of water was collected during the five quenches. The gas flow up the stack was apparently not uniform and the concentration of water droplets was probably not uniform across the tower cross section, however, for purposes of comparing this data to the 1976 data it is assumed that such uniformity exists. Based upon such an assumption, the quantity of water evaporated up the stack is given as:

$$\frac{\text{Quantity of Water Collected (ml)}}{\text{3785 ml/gal.}} \times \frac{(\text{Tower Diameter})^2}{(\text{Orifice Diameter})^2} = \text{gal/test}$$

For Test No. 1

$$\frac{137}{3785} \times \frac{(188.5)^2}{(0.56)^2} = 4100 \text{ gal/test}$$

$$\frac{\text{4100 gal/test}}{\text{5 quenches/test}} \times \frac{\text{8.34 lbs water}}{\text{gallon}} = 6838 \text{ lbs water/quench}$$

10.3 Mass Balance Around the Quench Tower

The basic functions of the quench tower are to quickly provide a

Table 10-5
Up-Stack Water Flow as Extrapolated from Cyclone, Condenser and Impinger Catch

		Water Catch (ml) per test				Quantity up-stack (pounds per quench)		Total Up-stack per quench	
Test No.	No. of Quenches per test	Cyclone	Condenser	Impinger	Silica Gel	Cyclone	Condenser plus Impinger plus silica gel	Gallons	Pounds
1	5	34	50	36	17	1698	5140	820	6838
2	5	36	160	76	2	1796	11876	1639	13672
2B	5	15	60	9	7	1544	7824	1123	9368
3	5	28	50	1	3	2883	5559	820	8433
4	5	12	28	3	10	1235	4221	654	5456
5	5	30	55	4	15	2426	5985	1009	8411
6	5	28	61	0	12	2883	7515	1247	10398
7	5	11	42	4	6	890	4206	611	5096
8	4	27	100	0	8	2114	8455	1267	10569
9	5	12	100	8	9	970	9463	1251	10433
10	4	17	50	0	10	1719	6066	933	7785
11	4	10	40	0	2	783	3288	488	4071
12	3	15	60	0	8	2022	9166	1341	11188
13	6	24	58	15	9	1618	5527	857	7145
14	5	18	50	0	7	1409	4463	704	5872
15	4	23	60	0	4	2325	6470	1266	10561
16	4	27	70	0	7	2730	7785	1261	10515
17	6	24	84	0	7	1617	6133	929	7750
						32662	119142	18220	153561
Average						1815	6619	1012	8531

large quantity of water to cool the incandescent coke below its ignition temperature, and to recover the excess water for re-use.

It is concluded in the 1976 Lorain report that the contaminants in the quench water primarily originated from two sources - the coke itself, and the flushing liquor which has been previously used to cool the gases produced by the coking process. Most of the volatile material present in the coal is driven off by the coking process. However, a certain amount of both organic and inorganic materials are introduced to the quench process by the coke. Some of these materials then enter the atmosphere during a subsequent quenching operation, some are to be found in the sludge which is removed from the sump and some are retained or readsorbed by the quenched coke. When process flushing liquor is used as a make up source for the quench water, additional contaminants are introduced because this flushing liquor was used to cool the gases produced during the coking operations.

In 1976 the makeup to the sump (Q_5) was 1900 gallons and the up stack flow was 1800 gallons per quench. Using these data a mass balance of the T.O.C. entering with makeup liquor and exiting the quench system can be constructed. The total organic carbon (T.O.C.) in water samples is summarized in Table 10-6. Makeup used during the contaminated tests had 50 times more T.O.C. than the relatively clean service water.

This mass balance (Table 10-6) reveals that of the organic compounds identified (PAH and polar) there was a larger quantity found in the stack emissions than was detected in the makeup water. It is apparent that these organics were introduced by the coke into the quench emissions in both the contaminated and clean tests, since there is 2 to 10 times as much PAH, and 10 to 500 times as much polar material in the emissions as would be expected from the amount introduced by the makeup water.

TABLE 10-6
MASS BALANCE OF ORGANIC COMPOUNDS
(grams per metric ton of coal)

	Clean	Contaminated
T.O.C. entering the quench process in the makeup water:	20	1,000
Polar Compounds	0.002	50
PAH	0.1	17
T.O.C. entering the quench process in the coke	NA	NA
Organic matter leaving the quench process in the stack gases:		
Polar Compounds	1	600
PAH	1	30
T.O.C. left in the coke	NA	NA
T.O.C. destroyed or formed in the quench	NA	NA
T.O.C. deposited in the sump sludge	NA	NA

NA = Not Available

The following mechanisms would account for the balance of the T.O.C.

- T.O.C. would be oxidized by the uncooled areas of incandescent coke.
- The cooled coke would have a large activated surface which would adsorb T.O.C.

11.0 SOURCE OF ORGANIC EMISSIONS

The two variables in the coke quenching process being investigated in this test program are the quality of quench makeup water ("clean" water from the Black River versus "contaminated" plant flushing liquor) and the quality of the coke being quenched (green coke versus nongreen coke). The 1976 EPA tests at Lorain(1) and tests conducted at Dominion Foundries and Steel(21) showed that the quality of quench water (concentration of total dissolved solids) had a definite effect on the concentration of air contaminants in the quench tower plume. But, the effect of water quality on organic emissions specifically, and any effect on these emissions produced by coke greenness had not been studied. As discussed in Section 6, this test program was designed to address the influence of these two parameters.

11.1 Statistical Analyses

Two types of statistical analyses were performed on the organic emissions data: analysis of variance and simple correlations. The following sets of data (in lbs/ton of coal) were used in the analyses:

1) Total PAH, all tests (15 tests)
2) Total PAH, clean water tests (11 tests)
3) Each organic compound, all tests
4) Each organic compound, clean water tests

For the analysis of variance for data from all tests (1 and 3 above), the following hypothesis was used:

> The effect of differences between the population means for the three groups is identical, that is $\mu_1 = \mu_2 = \mu_3$, where
>
> μ_1 represents the population mean of clean water - green coke
> For example:
> The sum of the PAH concentrations for each of the 5 clean water - green coke tests divided by 5

= the sample mean (which represents the population mean for clean water-green coke)

μ_2 represents the population mean of clean water-nongreen coke

μ_3 represents the population mean of contaminated water - nongreen coke

When data from the clean water tests only was analyzed, this hypothesis was used:

> The effect of differences between the two population means is identical, that is $\mu_1 = \mu_2$, where
>
> μ_1 and μ_2 are defined as above

In statistical terms, these hypotheses were rejected at the 10% significance level, indicating that there are less than ten chances in 100 that the effect of differences between the population means will be the same. The results of the analysis of variance are shown in Table 11-1. Significant relationships are defined as those where the different process conditions do not have the same effect on organic emissions, within 90% confidence limits. Such results are denoted with a star(s). The more stars appearing for a particular value, the more significant the relationship (see explanatory note at bottom of Table). It is obvious that the concentration of almost every species listed and total PAH are related to the process conditions of water quality and coke greenness. And, when the factor of water quality is held constant, the concentration of most compounds and of total PAH are related to coke greenness. Overall, the F values generated for all tests are higher and more significant than those for the clean water tests. This points out that in general, water quality has a greater effect on the concentration of these organic emissions than does coke greenness.

In order that the relationship of organic emissions to these two process conditions could be defined and better studied, simple correlations for these sets of data were also run.

TABLE 11-1
ANALYSIS OF VARIANCE - F VALUES (22)

Organic Species	All test conditions	Clean Water Tests
Total PAH	31.519***	18.621**
Naphthalene	19.662***	5.361**
Benzothiophene	35.425***	0.108
Methyl naphthalenes	24.820***	5.994**
Acenaphthalene/biphenylene	30.004***	9.372**
Biphenyl	20.830***	5.419**
Dimethyl naphthalenes	8.660***	11.258***
Fluorene	12.359***	7.268**
Dibenzofuran/methyl biphenyl	21.098***	4.197*
Anthracene/phenanthrene	19.445***	4.051*
Dibenzothiophene	15.229***	0.427*
Methyl anthracenes	7.435***	10.226**
Fluoranthene	15.832***	1.370
Pyrene	16.126***	5.044*
$C_{16} H_{12}$ PAH	4.367**	0.818
Methyl fluoranthene/methyl pyrene	8.743***	4.295*
Dihydrobenzofluorene	4.527**	0.002
Chrysene/benz(a)anthracenes	6.443***	0.446
3-methyl cholanthrene	0.275	0.015
Benzo(a) pyrene	6.558**	0.514
Pyridine	6.157**	0.668
Methyl pyridine	3.418*	1.235
Aniline	10.144***	0.045
Phenol	8.289***	0.112
Dimethyl/ethyl pyridine	5.731**	0.818
Toluidine	6.217**	0.818
Cresol	9.726***	1.360
Trimethyl pyridine	10.733***	1.227
Quinoline	9.160***	3.887*
Methyl quinoline	5.391**	0.108
Phthalates	51.524***	7.931**

*** Significant at 1% rejection level.

** Significant at 5% rejection level.

* Significant at 10% rejection level.

The average concentration of each organic compound for all tests was run versus

- Quench water quality (designated as clean or contaminated
- Coke greenness (using numerical ratings from 0 to 5)
- The average concentration of every other organic compound

The results of this analysis are presented in Table 11-2. Correlation values from 0.8 to 1.0 and from -0.8 to -1.0 are taken to be significant. The concentrations of some compounds for some tests were below the detection limits of the analytical procedures employed. In these cases a value of zero (0) was given to the data point; otherwise, the point would be excluded as though that species had never been tested for or analyzed. It should also be noted that the computer program for simple correlations could not handle all of the data at once, so the data were split into two parts. Because of this, there are no correlations listed between compounds on the first page and compounds on the second page of each table.

Table 11-2 reinforces the conclusion that water quality is a more dominant factor than coke greenness. Also, the positive correlation values for water indicate that for total PAH and for all compounds except 3-methyl cholanthrene (No. 20), the concentration of these organic emissions is higher when contaminated water is in use than when clean water is in use. There appears to be no correlation between coke greenness and organic emissions in Table 11-2. However, since water quality dominates over coke greenness, a true assessment of the influence of coke greenness cannot be made until the factor of water quality is excluded from the data.

The simple correlations analysis for evaluation of the effect of coke quality on organic emissions included correlations between the average concentration for clean water tests of each organic compound versus

- Coke greenness (using numerical ratings from 0 to 5)
- The average concentration of every other organic compound

Table 11-3 includes the results of this analysis and shows that the correlations between each compound and coke greenness are much higher here than when quench water is also considered (Table 11-2). Total PAH concentrations are plotted against coke greenness in Figure 11-1 and again a correlation appears between these two variables. Among the green (or nongreen) tests themselves, however, the correlation is not good. Also, the computer correlations do not fall into the "significant" range (0.8 to 1.0). The visual rating system for coke greenness is very useable but deviations of one unit in either direction may occur(1). This may account for the lower correlations.

11.2 Discussion

It has been shown that two sources of organic matter found in coke quench tower emissions are contaminated quench makeup water and green coke. The process that is common to both of these parameters is the coking of the coal. As described in Section 5, some of the gases, oils, and tars that are distilled from the coal during coking are combined with blowdown from other plant processes to produce flushing liquor (contaminated water) which is used to quench coke. The process of destructive distillation going on in the coke ovens could be the producer of PAH that is distilled off to mix with flushing liquor or trapped in the coke when this distillation has not been completed and the coke is "green". The formation of PAH in combustion processes has been studied(18), but PAH formation in an oxygen deficient atmosphere such as a coke oven has not been widely discussed in the literature. However, previous studies of coke oven charging emissions(23) and coke oven door emissions(24) have shown the presence of PAH compounds. It would seem reasonable, therefore, that the coking process itself may be the true source of organics which are later found in quench tower emissions.

TABLE 11-2

SIMPLE CORRELATIONS

(using water quality, coke greenness, individual organics, and total PAH values for all tests)

		WATER 2	COKE 3	NAPHTHAL 4	BENZOTHI 5	METHYLNA 6	ACENAPHT 7	BIPHENYL 8	DIMETHYL 9	FLUORENE 10	DIBENZOF 11	ANTHRACE 12
WATER	2	1.0000										
COKE	3	-0.6520	1.0000									
NAPHTHAL	4	0.8753	-0.6300	1.0000								
BENZOTHI	5	0.9247	-0.5668	0.8714	1.0000							
*METHYLNA	6	0.8963	-0.5103	0.8462	0.9905	1.0000						
ACENAPHT	7	0.9128	-0.6121	0.9789	0.9511	0.9163	1.0000					
BIPHENYL	8	0.8804	-0.4943	0.8201	0.9918	0.9895	0.9179	1.0000				
DIMETHYL	9	0.6080	-0.0060	0.5513	0.7163	0.7762	0.6519	0.7617	1.0000			
FLUORENE	10	0.8203	-0.4746	0.6624	0.8656	0.9069	0.7759	0.8619	0.6979	1.0000		
DIBENZOF	11	0.8820	-0.4994	0.8183	0.9920	0.9853	0.9158	0.9987	0.7521	0.8544	1.0000	
ANTHRACE	12	0.8736	-0.4919	0.8356	0.9785	0.9565	0.9167	0.9820	0.7418	0.7646	0.9851	1.0000
DIBENZOT	13	0.8469	-0.5091	0.8268	0.9610	0.9300	0.9026	0.9653	0.7002	0.7109	0.9703	0.9954
METHYLAN	14	0.6658	-0.1151	0.6102	0.8193	0.8220	0.7146	0.8529	0.9097	0.6383	0.8522	0.8795
FLUORANT	15	0.8510	-0.4699	0.7886	0.9539	0.9238	0.8748	0.9648	0.7054	0.7172	0.9685	0.9889
PHRENE	16	0.8512	-0.4749	0.8362	0.9292	0.8867	0.8921	0.9298	0.6692	0.6360	0.9337	0.9741
METHYL	17	0.7289	-0.2210	0.6716	0.8341	0.8283	0.7563	0.8683	0.7243	0.6077	0.8579	0.8910
DIHYDROB	18	0.6557	-0.4222	0.7221	0.7593	0.7178	0.7561	0.7605	0.5184	0.4559	0.7615	0.8021
CHRYSENE	19	0.7101	-0.5059	0.5932	0.7983	0.7715	0.6890	0.8169	0.5397	0.6492	0.8179	0.8285
METHYL3	20	-0.2060	0.0407	-0.2032	-0.2955	-0.2955	-0.2471	-0.3163	-0.2069	-0.2268	-0.3235	-0.3319
PHENOL	21	0.7616	-0.4492	0.7658	0.8638	0.8076	0.8181	0.8686	0.6064	0.5098	0.8773	0.9409
CRESOL	22	0.7864	-0.4061	0.6334	0.9008	0.8717	0.7532	0.9264	0.7001	0.7014	0.9330	0.9477
QUINOLIN	23	0.7773	-0.3894	0.5914	0.8928	0.8722	0.7251	0.9224	0.7112	0.7397	0.9282	0.9291
PHTHALAT	24	0.9423	-0.6139	0.9158	0.8270	0.7748	0.8944	0.7653	0.5174	0.6185	0.7693	0.7987
BENZO	25	0.7096	-0.4561	0.6116	0.7855	0.7854	0.7034	0.7773	0.5000	0.7629	0.7883	0.7541

		DIBENZOT 13	METHYLAN 14	FLUORANT 15	PHRENE 16	METHYL 17	DIHYDROB 18	CHRYSENE 19	METHYL3 20	PHENOL 21	CRESOL 22	QUINOLIN 23
DIBENZOT	13	1.0000										
METHYLAN	14	0.8660	1.0000									
FLUORANT	15	0.9904	0.8744	1.0000								
PHRENE	16	0.9821	0.8463	0.9840	1.0000							
METHYL	17	0.8843	0.8758	0.9157	0.9084	1.0000						
DIHYDROB	18	0.8190	0.6935	0.8369	0.8452	0.7713	1.0000					
CHRYSENE	19	0.8336	0.7124	0.8242	0.7945	0.7369	0.5552	1.0000				
METHYL3	20	-0.3332	-0.2169	-0.2714	-0.2864	-0.2293	0.1239	-0.4661	1.0000			
PHENOL	21	0.9638	0.8246	0.9590	0.9792	0.8750	0.8491	0.7730	-0.3058	1.0000		
CRESOL	22	0.9487	0.8709	0.9689	0.9273	0.8838	0.7531	0.8382	-0.3224	0.9200	1.0000	
QUINOLIN	23	0.9239	0.8629	0.9489	0.8925	0.8642	0.7118	0.8345	-0.3190	0.8768	0.9950	1.0000
PHTHALAT	24	0.7863	0.5905	0.7791	0.8339	0.6685	0.6703	0.6221	-0.1701	0.7606	0.6663	0.6296
BENZO	25	0.7301	0.6224	0.7137	0.6535	0.5762	0.5607	0.5609	-0.0915	0.6078	0.7105	0.7232

		PHTHALAT 24	BENZO 25
PHTHALAT	24	1.0000	
BENZO	25	0.5455	1.0000

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* See the Key to Tables 11-2 and 11-3.

TABLE 11-2 continued - SIMPLE CORRELATIONS

		WATER 2	COKE 3	C16H12PA 4	PYRIDINE 5	METHYLPY 6	ANILINE 7	DIMETHYL 8	TOLUIDIN 9	TRIMETHY 10	METHYLQU 11
WATER	2	1.0000									
COKE	3	-0.6520	1.0000								
C16H12PA	4	0.6478	-0.3017	1.0000							
PYRIDINE	5	0.7117	-0.3302	0.9736	1.0000						
METHYLPY	6	0.6022	-0.2279	0.9798	0.9635	1.0000					
ANILINE	7	0.7927	-0.4093	0.9418	0.9868	0.9138	1.0000				
DIMETHYL	8	0.6989	-0.3366	0.9095	0.9739	0.8929	0.9751	1.0000			
TOLUIDIN	9	0.7134	-0.3369	0.9682	0.9458	0.9545	0.9297	0.8517	1.0000		
TRIMETHY	10	0.8008	-0.4422	0.8180	0.9107	0.7696	0.9574	0.9590	0.7916	1.0000	
METHYLQU	11	0.6876	-0.3338	0.9626	0.9696	0.9697	0.9451	0.9151	0.9527	0.8336	1.0000

		WATER 2	COKE 3	TOTAL PAH 4
WATER	2	1.0000		
COKE	3	-0.6520	1.0000	
TOTAL PAH	4	0.9163	-0.6017	1.0000

TABLE 11-3

SIMPLE CORRELATIONS

(using coke greenness, individual organics, and total PAH values for clean water tests only)

		COKE 2	NAPHTHAL 3	BENZOTHI 4	METHYLNA 5	ACENAPHT 6	BIPHENYL 7	DIMETHYL 8	FLUORENE 9	DIBENZOF 10	ANTHRACE 11	DIBENZOT 12
COKE	2	1.0000										
NAPHTHAL	3	0.6350	1.0000									
BENZOTHI	4	0.2165	-0.1152	1.0000								
METHYLNA	5	0.6902	0.9329	0.0109	1.0000							
ACENAPHT	6	0.7076	0.9077	-0.0872	0.8114	1.0000						
BIPHENYL	7	0.5877	0.7284	0.0846	0.6160	0.9212	1.0000					
DIMETHYL	8	0.7106	0.5762	-0.0056	0.5997	0.4095	0.1695	1.0000				
*FLUORENE	9	0.7393	0.7412	0.4632	0.7975	0.7466	0.7512	0.4523	1.0000			
DIBENZOF	10	0.5570	0.0579	0.3280	0.0759	0.4112	0.6143	-0.0677	0.4754	1.0000		
ANTHRACE	11	0.6308	0.3634	0.7327	0.5137	0.3266	0.3197	0.5101	0.7211	0.3311	1.0000	
DIBENZOT	12	-0.2000	-0.3132	0.6151	-0.2127	-0.2890	-0.0716	-0.1963	0.1280	0.1777	0.5435	1.0000
METHYLAN	13	0.7094	0.5349	0.1568	0.5703	0.4295	0.2392	0.9013	0.5051	0.0771	0.7195	0.1239
FLUORANT	14	0.3366	0.4441	-0.1604	0.2874	0.6812	0.6853	-0.0024	0.3394	0.4780	0.0661	-0.1095
PHRENE	15	0.5344	0.6154	-0.0881	0.4929	0.8180	0.8806	0.2406	0.5516	0.5862	0.1699	-0.1128
METHYL	16	0.5848	0.9254	-0.0651	0.8773	0.9420	0.8310	0.3652	0.7164	0.2228	0.3996	-0.1543
DIHYDROB	17	-0.0391	0.0693	-0.4653	-0.0550	0.1614	0.0410	-0.0448	-0.3189	-0.1280	-0.3977	-0.5301
CHRYSENE	18	-0.3046	-0.1752	0.4598	-0.1726	-0.1101	0.1591	-0.2146	0.1213	0.0637	0.2473	0.6508
METHYL3	19	-0.0832	0.0911	-0.5272	-0.0416	0.1045	-0.0737	0.0724	-0.3189	-0.2257	-0.2727	-0.2718
PHENOL	20	0.0377	0.0913	-0.2664	-0.1405	0.3412	0.4822	-0.2951	-0.0666	0.3948	-0.3622	-0.2942
CRESOL	21	0.2835	0.3049	-0.1753	0.0470	0.6122	0.7529	-0.1169	0.2406	0.6291	-0.1509	-0.2019
QUINOLIN	22	0.4205	0.3560	-0.2651	0.0770	0.5420	0.5531	0.3578	0.1677	0.3877	-0.0635	-0.3023
PHTHALAT	23	0.5127	0.1094	-0.0333	0.0522	0.3021	0.3517	0.5160	0.1847	0.4655	0.1822	-0.0876
BENZO	24	-0.1026	-0.3633	0.2953	-0.2609	-0.3030	-0.3521	-0.3086	-0.2271	0.0334	0.1515	0.2205

		METHYLAN 13	FLUORANT 14	PHRENE 15	METHYL 16	DIHYDRUB 17	CHRYSENE 18	METHYL3 19	PHENOL 20	CRESOL 21	QUINOLIN 22	PHTHALAT 23
METHYLAN	13	1.0000										
FLUORANT	14	0.2002	1.0000									
PHRENE	15	0.3171	0.7525	1.0000								
METHYL	16	0.4471	0.6172	0.6556	1.0000							
DIHYDROB	17	-0.0261	0.4867	0.1221	0.1612	1.0000						
CHRYSENE	18	-0.0984	-0.0834	0.0054	-0.0412	-0.3230	1.0000					
METHYL3	19	0.2092	0.5746	0.1521	0.1560	0.8159	-0.3897	1.0000				
PHENOL	20	-0.2731	0.4411	0.5955	0.2059	0.5012	-0.0891	0.2330	1.0000			
CRESOL	21	-0.0571	0.7415	0.8985	0.4088	0.2729	-0.0050	0.1832	0.7992	1.0000		
QUINOLIN	22	0.3380	0.5855	0.8412	0.3131	0.3062	-0.0999	0.3129	0.5540	0.8219	1.0000	
PHTHALAT	23	0.4515	0.2067	0.4608	0.0945	0.0554	0.2102	-0.0529	0.1841	0.4020	0.6731	1.0000
BENZO	24	-0.0808	0.1487	-0.3546	-0.2162	0.0933	-0.2236	0.2593	-0.3256	-0.2374	-0.3555	-0.4054

		BENZO 24
BENZO	24	1.0000

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* See the Key to Tables 11-2 and 11-3.

TABLE 11-3 continued - SIMPLE CORRELATIONS

		COKE 2	C16H12PA 3	PYRIDINE 4	METHYLPY 5	ANILINE 6	DIMETHYL 7	TOLUIDIN 8	TRIMETHY 9	METHYLOU 10
COKE	2	1.0000								
C16H12PA	3	-0.2649	1.0000							
PYRIDINE	4	-0.3539	-0.1083	1.0000						
METHYLPY	5	0.2376	-0.1005	-0.1073	1.0000					
ANILINE	6	-0.0848	-0.1439	0.8808	-0.1416	1.0000				
DIMETHYL	7	-0.3902	-0.1000	0.9970	-0.0992	0.8412	1.0000			
TOLUIDIN	8	-0.3902	-0.1000	0.9970	-0.0992	0.8412	1.0000	1.0000		
TRIMETHY	9	0.4870	-0.1000	-0.0221	-0.0970	0.4539	-0.1000	-0.1000	1.0000	
METHYLOU	10	-0.1668	-0.1397	-0.1514	0.3703	-0.2011	-0.1397	-0.1397	-0.1397	1.0000

		COKE 2	TOTAL PAH 3
COKE	2	1.0000	
TOTAL PAH	3	0.8374	1.0000

KEY TO TABLES 11-2 AND 11-3
SIMPLE CORRELATIONS

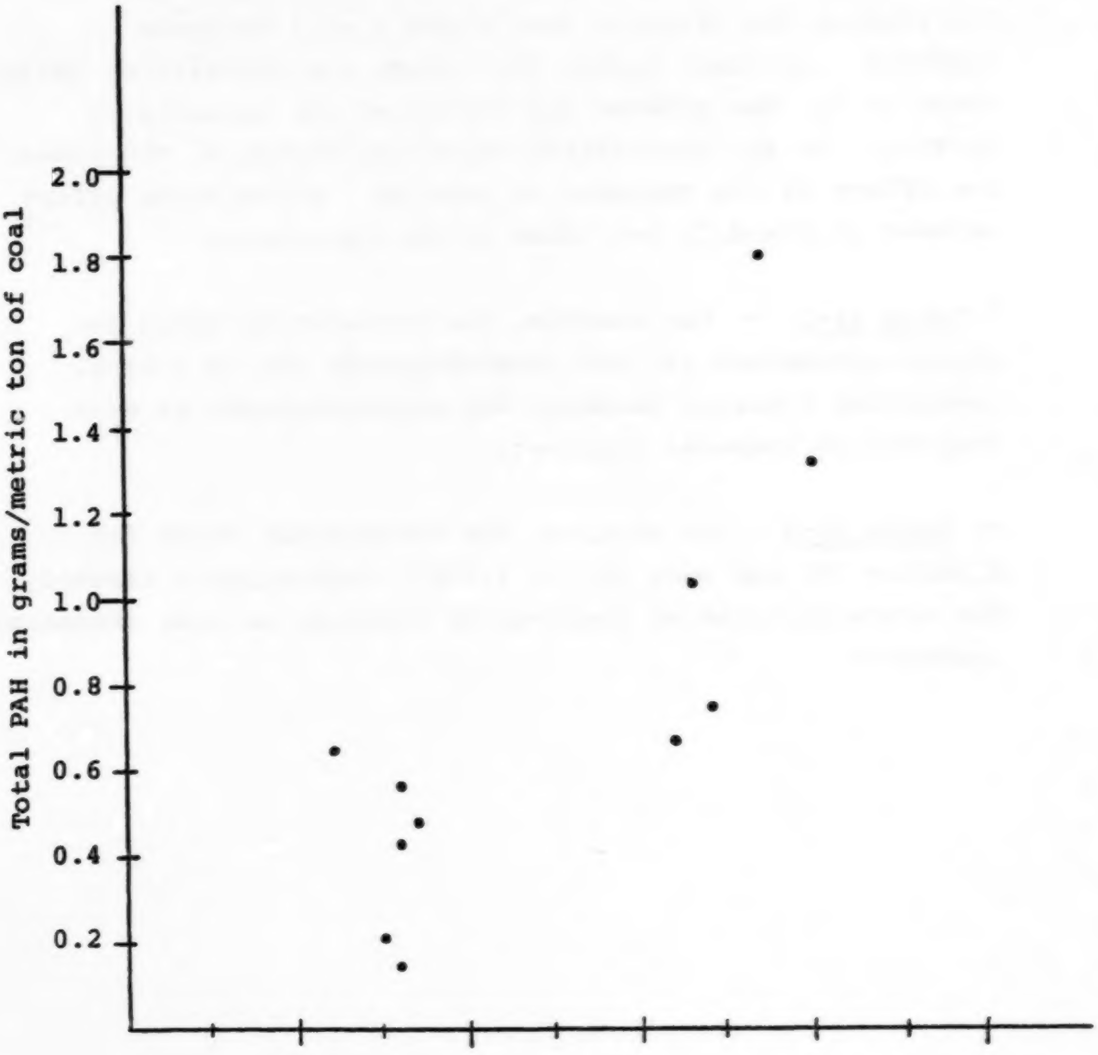
The correlation value indicates the relationship between two variables. As a positive correlation value approaches +1, the greater the tendency that x and y will increase together. As a negative correlation value approaches -1, the greater the tendency that x and y will decrease together. In other words, the closer the correlation value comes to ±1, the greater the effect of one variable on another. As any correlation value approaches 0, the lesser the effect of one variable on another. Correlation values between ±0.8 and ±1 are taken to be significant.

* Table 11-2 - For example, the correlation value for methylnaphthalene (6) and benzothiophene (5) is 0.9905, indicating a strong tendency for concentrations of each compound to increase together.

** Table 11-3 - For example, the correlation value for fluorene (9) and coke (2) is 0.7393, indicating a tendency for concentrations of fluorene to increase as coke greenness increases.

FIGURE 11-1

GRAPH OF
TOTAL PAH VERSUS COKE GREENNESS
FOR THE CLEAN WATER TESTS



Benzo (a) pyrene is often used as an indicator for the presence of other carcinogenic compounds(23) and subsequently as an indicator for PAH. Though BaP may be representative of the presence of PAH, the subject study showed that although BaP levels did correlate well with water quality they did not correlate with coke greenness or with other PAH compounds.

The presence of phthalates in the quench tower samples was originally judged to be contamination. However, substantial concentrations of phthalate have been reported in coke oven door emissions(24). Also, the analysis of variance and simple correlations do show phthalate concentration to increase substantially when contaminated water and/or green coke is in use.

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APPENDIX A

SUMMARY OF COKE QUENCH EMISSION SAMPLING DATA

SUMMARY OF COKE QUENCH EMISSION SAMPLING DATA

TEST NO.	1	2	2B	3	4	5	6	7	8
DATE	11/3/77	11/4/77	11/5/77	11/4/77	11/6/77	11/7/77	11/6/77	11/8/77	11/8/77
TIME PERIOD	1600-1630	1440-1444	1205-1240	1357-1620	1333-1646	1158-1250	1422-1430	1012-1050	1219-1250
POSITION IN STACK	B1	B1	B1	B1	B1	B1	B1	B1	B1
NUMBER QUENCHES SAMPLED	5	5	5	5	5	5	5	5	4
NET SAMPLING TIME (MIN.)	12.3	14.3	12.1	11.6	12.1	12.9	11.9	12.4	9.4
FLOW PARAMETERS									
NET % ISOKINETIC	101	109	108	102	96	97	109	98	98.1
MEAN VERTICAL VELOCITY (fpm)	1445	1755	1469	1583	1224	1244	1582	1133	1428
MEAN STACK TEMPERATURE (°F)	175	175	175	175	175	175	175	175	175
MEAN VOLUMETRIC FLOW (SCFM)	189287	201588	173382	205145	159993	149295	193104	145886	152725
% MOISTURE BY VOLUME	19.0	28.9	27.0	19.8	19.2	25.7	24.5	20.4	33.9
MOLECULAR WEIGHT OF STACK GAS	26.8	25.7	25.9	26.7	26.7	26.02	26.26	26.6	25.1
MOLE FRACTION OF DRY GAS	0.81	0.71	0.73	0.80	0.81	0.74	0.75	0.79	0.66
GAS ANALYSIS (DRY PERCENT BASIS)									
CARBON DIOXIDE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
OXYGEN	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
CARBON MONOXIDE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
NITROGEN	80.0	80.0	80.0	80.0	80.0	80.0	80.0	80.0	80.0
SAMPLING TRAIN PARAMETERS									
NOZZLE DIAMETER (in.)	0.56	0.56	0.39	0.39	0.39	0.44	0.39	0.44	0.50
PITOT TUBE CORRECTION FACTOR	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
VOLUME OF DRY GAS SAMPLED (SCFD)	20.78	27.65	9.70	10.41	7.95	10.17	10.69	9.67	9.96
VOLUME OF WATER COLLECTED:									
CYCLONE - DROPLETS (ml)	34	36	15	28	12	30	28	11	27
CONDENSER - VAPOR (ml)	50	160	60	50	28	55	61	42	100
IMPINGERS - VAPOR (ml)	36	76	9	1	2	4	0	4	0
SILICA GEL - VAPOR (ml)	17	2	7	3	10	15	12	6	8
SUBTOTAL - VAPOR (ml)	103	238	76	54	40	74	73	52	108
TOTAL (ml)	137	274	91	92	52	104	101	63	135

SUMMARY OF COKE QUENCH EMISSION SAMPLING DATA

TEST NO.	9	10	11	12	13	14	15	16	17
DATE	11/8/77	11/8/77	11/9/77	11/9/77	11/15/77	11/17/77	11/19/77	11/19/77	11/19/77
TIME PERIOD	1344-1415	1619-1655	1029-1240	1233-1420	1206-1413	1159-1240	1444-1435	1640-1612	1438-1439
POSITION IN STACK	B1	B1	B1	A1	B1	B1	B1	A1	B1
NUMBER QUENCHES SAMPLED	5	4	4	3	6	5	4	4	6
NET SAMPLING TIME (MIN.)	12.1	9.6	10.1	8.2	14.8	13.5	9.7	9.7	15.8
FLOW PARAMETERS									
NET % ISOKINETIC	138	106	86	105	91	70	98	109	89
MEAN VERTICAL VELOCITY (fpm)	1575	1337	1253	1373	135	1415	1414	1419	1459
MEAN STACK TEMPERATURE (^{o}F)	175	175	175	175	175	175	175	175	175
MEAN VOLUMETRIC FLOW (SCFM)	165575	164733	170344	153179	166719	188192	169542	166213	179708
% MOISTURE BY VOLUME	35.0	23.8	15.9	31.0	24.1	17.7	25.8	27.5	23.8
MOLECULAR WEIGHT OF STACK GAS	25.0	26.2	27.1	25.5	26.2	26.9	26.0	25.8	26.2
MOLE FRACTION OF DRY GAS	0.65	0.76	0.84	0.69	0.76	0.82	0.74	0.72	0.76
GAS ANALYSIS (DRY PERCENT BASIS)									
CARBON DIOXIDE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
OXYGEN	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
CARBON MONOXIDE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
NITROGEN	80.0	80.0	80.0	80.0	80.0	80.0	80.0	80.0	80.0
SAMPLING TRAIN PARAMETERS									
NOZZLE DIAMETER (in.)	0.44	0.44	0.50	0.44	0.44	0.50	0.44	0.44	0.44
PITOT TUBE CORRECTION FACTOR	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
VOLUME OF DRY GAS SAMPLED (SCFD)	10.30	9.11	10.43	7.15	12.28	12.47	8.74	9.56	13.77
VOLUME OF WATER COLLECTED:									
CYCLONE - DROPLETS (ml)	12	17	10	15	24	18	23	27	24
CONDENSER - VAPOR (ml)	100	50	40	60	58	50	60	70	84
IMPINGERS - VAPOR (ml)	8	0	0	0	15	0	0	0	0
SILICA GEL - VAPOR (ml)	9	10	2	8	9	7	4	7	7
SUBTOTAL - VAPOR (ml)	117	60	42	68	82	57	64	77	91
TOTAL (ml)	129	77	52	83	106	75	87	104	115

APPENDIX B

GASEOUS EMISSIONS - 1976 LORAIN STUDY

TABLE B-1

GASEOUS EMISSIONS - 1976 LORAIN STUDY[1]
(ppm by weight)

	Clean Quench Water	Contaminated Quench Water
Oxygen		115,402
Carbon Dioxide		16,806
Carbon Monoxide		681
Total Hydrocarbon		12 (by volume)
Sulfur Dioxide	2.2	187
Sulfide	0.003	0.003

Note: The concentration of these gases in the quench tower emission was determined by the following methods:

	Sampling -	Analysis
Oxygen	Grab flask -	Orsat 40
Carbon Dioxide	Grab flask -	Orsat 40
Carbon Monoxide	Grab flask -	Gas Chromatography
Total Hydrocarbon	Grab flask -	Gas Chromatography
Sulfur Dioxide	EPA 6 Train with moisture trap -	EPA 6
Sulfide	EPA 6 Train with moisture trap -	EPA 6

APPENDIX C

CALCULATIONS

CALCULATIONS

Nomenclature used:

An_i = Area nozzle used at each point - Sq. Ft.
Fs = Pitot tube factor
MD = Mole fraction dry gas
P_b = Barometric Pressure - In. Hg. abs.
P_m = Average orifice pressure drop - In. H_2O
P_{mi} = Orifice pressure drop at one point - In. H_2O
P_s = Stack Pressure - In. Hg. abs.
T_m = Average gas meter temperature - °F
T_{m_i} = Gas meter temperature at one point - °F
T_{s_i} = Stack temperature at one point - °F
T_{t_i} = Elapsed sampling time for one point - Min.
V_m = Volume of dry gas sampled at meter conditions - $Ft.^3$
V_{m_i} = Dry gas meter reading at the end of a point - $Ft.^3$
V_w = Total volume of water collected - ml.
ΔP_i = Velocity pressure at one point - In. H_2O
N = Number of Quenches Tested

Other parameters are developed and defined in the calculations.

In order to calculate micrograms per cubic meter and grams per metric ton of coal, the following calculations are required:

Starting with the sample weight of the sample collected in some component of the stack gas sample train (modified EPA Method 5),

1) $$\frac{\mu g}{m^3} = \frac{\mu g\ \text{sample}}{V_{scfd}} \times \frac{\text{scfd}}{0.02832\ \text{scmd}}$$

2) $$\frac{\text{grams}}{\text{metric ton of coal}} = \frac{\text{grams sample}}{V_{scfd}} \times$$

$$\text{dscfm} \times \frac{\text{min}}{\text{quench}} \times \frac{\text{quench}}{11.9\ \text{metric tons of coal}}$$

where:

V_{scfd} = Volume of dry gas sampled

DSCFM = Mean volumetric flow of stack gas

11.9 metric tons of coal is the nominal tonnage charged per battery and therefore is equivalent to the coke quenched in any one quench.

Starting with the concentration of a parameter in μg/L as determined in a water sample,

$$\frac{\mu g/L \times 1900 \times 3.785}{11.9 \times 1{,}000{,}000} = \text{grams per metric ton of coal}$$

where:

1900 is the gallons of makeup (either service water or liquor) added to the quench tower sump during each quench. Also the quantity of water up the stack plus any other losses.

3.785 converts gallons to liters

1,000,000 converts μg to g.

Calculations for Particulates (EPA Method 5):

1. Volume of water vapor @ 70°F and 29.92 In. Hg. - $Ft.^3$

$$V_{w_{std}} = 0.0474 \times V_w$$

2. Volume of dry gas sampled at Standard Conditions - 70°F, 29.92" Hg. - $Ft.^3$

$$V_{m_{std}} = \frac{17.71 \times V_m \left(\frac{P_b + P_m}{13.6}\right)}{T_m + 460}$$

3. Percent Moisture in Stack Gas

$$\% M = \frac{V_{w_{std}}}{V_{m_{std}} + V_{w_{std}}} \times 100.$$

4. Average Molecular weight of Dry Stack Gas

$$MW_d = .44 \times \% CO_2 + .28 \times \% N_2 + .32 \times \% O_2 + .28 \times \% CO$$

5. Molecular Weight of Stack Gas

$$MW = MW_d \times \left(1. - \frac{\% M}{100}\right) + 18 \times \frac{\% M}{100}$$

6. Stack Velocity at Stack Conditions at one point - FPS

$$V_{s_i} = 85.48 \times F_s \sqrt{\frac{(T_{s_i} + 460) \times \Delta P_i}{P_s \times MW}}$$

7. Volume Water Collected at one point - ml.

$$W_{Liq_i} = \frac{V_{m_i} - V_{m(i-1)}}{V_m} \times V_w$$

8. Percent Isokinetic at one point

$$\%I_i = 1.667 \frac{\left(.00267 \times W_{Liq_i} + V_{m_i} - V_{m(i-1)} \frac{P_b + \frac{P_{m_i}}{13.6}}{(T_{m_i} + 460)}\right)\left(\frac{T_{s_i}}{P_s}\right)}{T_{t_i} \times V_{s_i} \times A_{n_i}}$$

9. Stack Velocity at Stack Conditions for one Nozzle - FPS

$$V_{s_{noz}} = 85.48 \times CP \times \frac{\sum_{i=1}^{n} \sqrt{\frac{\Delta P_i \times (T_{s_i} + 460)}{P_s \times MW}}}{n}$$

10. Volume Water Collected for one Nozzle - Ft.^{3}

$$W_{Liq_{noz}} = \frac{V_{m_i} - V_{m_1}}{V_m} \times V_w$$

11. Percent Isokinetic for one Nozzle

$$\%I_{noz} = 1.667 \frac{.00267 \times W_{Liq_{noz}} + V_{m_i} - V_{m_i}\left(\frac{P_b + \frac{\sum_{i=1}^{n}}{n} \frac{P_{m_i}}{13.6}}{(T_{m_i} + 460)/n}\right)}{\frac{\sum_{i=1}^{n}}{n}\left(T_{t_i} \times V_{s_i} \times A_{n_i}\right)} \times$$

$$\frac{\sum_{i=1}^{n}}{n}\left(\frac{T_{s_i}}{P_s}\right)$$

12. Stack Velocity at Stack Conditions Average - FPS

$$V_{s_{ave}} = 85.48 \times F_s \times \left(\frac{\sum_{i=1}^{n}}{n} \sqrt{\frac{\Delta P_i \times (T_{s_i} + 460)}{P_{s_i} \times MW}}\right)$$

13. Volume Water Collected for one Nozzle - ml.

$$W_{Liq_{Ave}} = \frac{V_{m_i} - V_{m_1}}{V_m} \times V_w$$

14. Percent Isokinetic Average

$$\%I_{Ave} = \sum \%I_{noz} \times \frac{V_{m_i} - V_{m_1}}{V_{m_n} - V_{m_1}}$$

15. Actual Gas Flow Rate @ Stack Conditions - ACFM

$Q_{stk} = 60 \times V_{s_{Ave}} \times$ Area of Stack

16. Gas Flow Rate Dry @ Standard Conditions - SCFMD

$$Q_s = 1062.6 \times V_{s_{Ave}} \times \frac{P_s}{T_s + 460} \times MD \times \text{Area of Stack}$$

17. Particulate emissions in grains per standard cubic feet Dry - (Gr/SCFD)

$GRD = .0154 \times Wt/V_{m_{std}}$

18. Particulate emissions in grains per standard cubic feet Dry adjusted to 12% CO_2 - (Gr/SCFD @ 12% CO_2)

$GRD' = GRD \times 12./\% \; CO_2$

19. Particulate emissions in grains per actual cubic feet - (Gr/ACF)

$$G = 17.71 \times GRD \times \frac{P_s \times MD}{(T_s + 460)}$$

20. Particulate emissions in pounds per hour (Lbs./Hr.)

$P = .008572 \times GRD \times Q_s$

21. Particulate emissions in pounds per process unit (Lb/process unit)

$P_m = P/(\text{process unit})$